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A Study of the Effect of Hydrogen Bonding upon the Infrared Absorption of the Hydroxyl Group

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THE recent work of Hendricks, Wulf, Hilbert and Liddell showing that the first harmonic is absent in the infrared absorption spectrum of the hydroxyl group when a hydrogen bond is formed, has emphasized the fact that infrared spectroscopy is a very promising method of studying solutions.[1]

Not the least important of the contributions of these authors is the technique of observing the infrared absorption of substances in dilute solution in an inert solvent. The term inert as used here really has a double significance. For example, it is desirable that the solvent absorb as little as possible and this condition will be fulfilled if the fundamental frequencies of the solvent lie well below (or above) the frequencies being used. What is still more important, however, is that in a solvent such as carbon tetrachloride many molecules show absorption bands which differ only slightly from those observed for the vapor. One would infer from this behavior that not only is there no tendency toward solvation but that the force field surrounding the solvent molecules must exert very weak influence on the solute molecules. Under these conditions one would anticipate only a slight shift in frequency and the more or less complete disappearance of the rotational envelope.

The work of Wulf *et al.* was limited by the use of a glass spectrograph so that they could not investigate the fundamental bands for the hydroxyl group. Since it was of great interest to determine what effect, if any, could be noted in the fundamental absorption, the authors have undertaken this investigation. A preliminary note[2] was published in this journal pointing out that, instead of disappearing, the fundamental was shifted to longer wave-lengths with increased intensity, and that there were indications that the amount of the shift was somewhat different in the case of intermolecular bonding from that for intramolecular bonding.

It should be emphasized at this point that the authors are using the term hydrogen bond in the traditional sense only, without implying any particular significance to the term bond. The fact is that a linkage may take place through a hydroxyl group causing the association of two molecules, or in the case of a single molecule forming a chelate ring when the configuration is favorable as has been pointed out by Wulf *et al.*[3] This linkage requires an energy of several kilocalories and is not to be explained by dipole interaction alone. Even if no such linkage is formed, there is reason to believe that the presence of certain groups in a position adjacent

[1] G. E. Hilbert, O. R. Wulf, S. B. Hendricks, and U. Liddell, J. Am. Chem. Soc. **58**, 548 (1936). W. M. Latimer and W. H. Rodebush, J. Am. Chem. Soc. **42**, 1419 (1920). W. H. Rodebush, Chem. Rev. **19**, 59 (1936). M. L. Huggins, J. Org. Chem. **1**, 407 (1936).

[2] A. M. Buswell, V. Deitz and W. H. Rodebush, J. Chem. Phys. **5**, 84 (1937).

[3] O. R. Wulf, U. Liddell and S. B. Hendricks, J. Am. Chem. Soc. **58**, 2287 (1936).

to the hydroxyl group may cause an observable shift in frequency. There are thus possible all degrees of interaction and any which causes an observable shift in frequency may be regarded as an incipient bond.

It is proposed here to present in some detail the evidence upon which the preliminary note was based.

The spectrographic equipment used is of conventional design. A 75 mm rocksalt prism is used with a Littrow mounting. The source of radiation is a Nernst glower and the thermocouple is directly connected to a Leeds-Northrup type HS galvanometer of unusually high sensitivity. The instrument was calibrated by locating the characteristic absorption bands of carbon dioxide, water vapor, benzene, etc.

The technique of Wulf and collaborators was followed. The absorption cell contains two compartments, one filled with pure solvent and the other with a dilute solution of substance to be investigated. By shifting the cell the two sides are placed in the beam in alternation and the galvanometer deflections d_0 and d are recorded. We have plotted the absorption curve log (d_0/d) against wave numbers, but the absorption is in general for an arbitrary quantity of substance. We have not reduced it to a molal basis as did Wulf and his collaborators.

Intramolecular Hydrogen Bonds

Our first studies were made upon substances of the type of *o*-nitrophenol and methyl salicylate in which compounds, as has been pointed out by Wulf *et al.*, there is reason to suspect the formation of a chelate ring through the hydrogen of the hydroxyl. In many of these substances there is also the possibility of a quinoid structure and the salts are believed to exist largely in this form by organic chemists. The free acids, however, are commonly assumed to exist in the normal benzenoid configuration.

Our first observations on these molecules revealed a very strong absorption at about 3350 wave numbers (3.0μ) which appeared to be distinct from the characteristic C–H absorption at slightly longer wave-lengths. This fact seemed to be so important that we proceeded to examine a number of different compounds of this type.

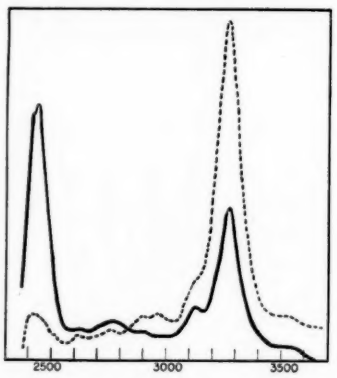

Fig. 1. Absorption curves for a dilute solution of *o*-nitrophenol in carbon tetrachloride. The solid line represents *o*-nitrophenol which has been treated with pure deuterium oxide. The dotted line represents the absorption curve obtained after the solution was allowed to stand for 30 minutes in contact with water vapor.

The list of those studied included: *o*-nitrophenol, 2.4 dinitro resorcinol, 2.4 dinitrophenol, 2.6 dinitrophenol,[2, 4, 6] trinitrophenol, methyl salicylate, and salicylaldehyde. The strong absorption peak was observed in every case in these compounds. In order to eliminate the effect of solvent, the absorption of *o*-nitrophenol was studied in carbon bisulfide and tetrachlor-ethylene. The results proved independent of the solvent used. An examination was made of the absorption of compounds closely related in type to the above, but having no possibility of hydrogen bonding. Typical molecules studied were paranitrophenol and *o*-nitroanisol. The results on these molecules indicated that the strong absorption peak could not be due to carbon hydrogen linkages, but a more positive proof was, of course, necessary.

It is generally assumed the exchange reaction of hydrogen with deuterium will take place readily with the hydroxyl hydrogen, and not at all, in the absence of catalysts, with the hydrogens attached to carbon. We have accordingly treated *o*-nitrophenol and other substances of this type with pure deuterium oxide for a few minutes and then removed the water by distillation in vacuum. The deuterated substance was then dissolved in dry carbon tetrachloride and the absorption curve determined. The solution was then allowed to stand in a closed vessel in contact with air saturated with water vapor for thirty minutes, at the end of which time the absorption curve was again determined. These

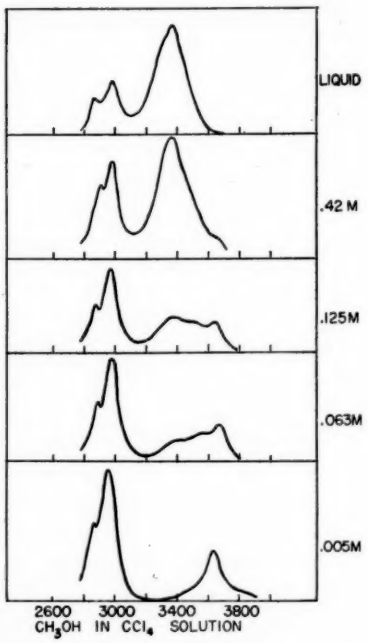

FIG. 2. Absorption curves for methyl alcohol at various concentrations in carbon tetrachloride and (top) pure liquid methyl alcohol.

curves show that a very considerable substitution of hydrogen by deuterium had taken place which was completely removed by thirty minutes exposure to water vapor (Fig. 1).

It is evident that a very rapid exchange is taking place and it is commonly accepted that this exchange can involve only the hydroxyl hydrogen. We are, of course, accepting the conclusions of others on this point, except for a single experiment with *o*-nitroanisol. There appears to be no exchange with this compound. Negative results with this compound, however, are not of great significance since it does not show the strong absorption at 3.0μ characteristic of the substances discussed above. When *o*-nitrophenol or methylsalicylate is treated with heavy water a considerable exchange takes place and the strong absorption peak at 3.0μ is greatly decreased in intensity and a new peak appears at 2440 wave numbers (4.1μ).[4] This is the amount of shift to be anticipated on the replacement of the hydroxyl hydrogen by deuterium. It is possible, of course, that the hydrogens in the positions *ortho* or *para* to the hydroxyl might be activated to such an extent as to permit a deuterium exchange. However, one would not expect the frequencies to be the same as for hydroxyl.

[4] In our original note this was incorrectly stated to be 4.2μ.

INTERMOLECULAR HYDROGEN BONDS

In our original note we indicated that we had obtained evidence that the absorption frequency for an intermolecular hydrogen bond was slightly different from that for an intramolecular hydrogen bond. It was pointed out to one of us by Dr. R. Bowling Barnes that, if our interpretation of our results was correct, many substances must be assumed to be completely hydrogen bonded in the pure liquid state, since the absorption band attributed to the hydroxyl is found in the neighborhood of 3400 cm^{-1}, whereas in the vapor state or in dilute solution the hydroxyl band appears at or near 3700 cm^{-1}.[5] The curves for the alcohols which we reproduce herewith are in complete agreement with this hypothesis and show a progressive shift of absorption with concentration.

We have investigated a number of alcohols at concentrations ranging from the dilute solutions to the pure liquid state. For the solutions of different concentrations cells of the same cross section, but of varying lengths, were used and the concentrations were adjusted so that the total amount of solute was constant. This was

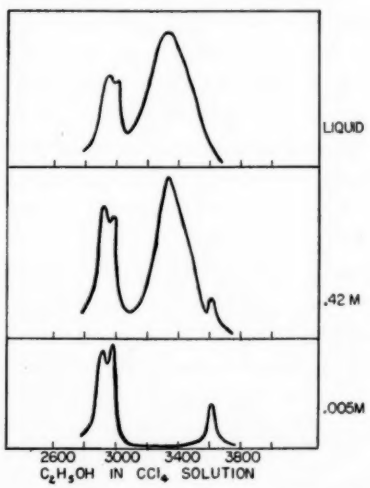

FIG. 3. Absorption curves for ethyl alcohol.

[5] Since the appearance of our preliminary note, there has come to our attention a note by Errera and Mollet, Nature **138**, 882 (1936), in which results are reported on the alcohols which are substantially the same as those reported here.

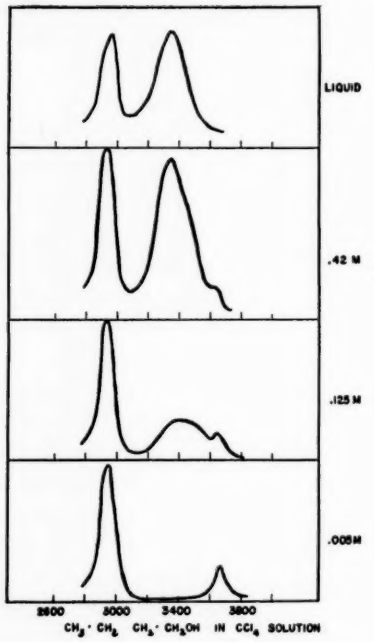

FIG. 4. Absorption curves for normal butyl alcohol.

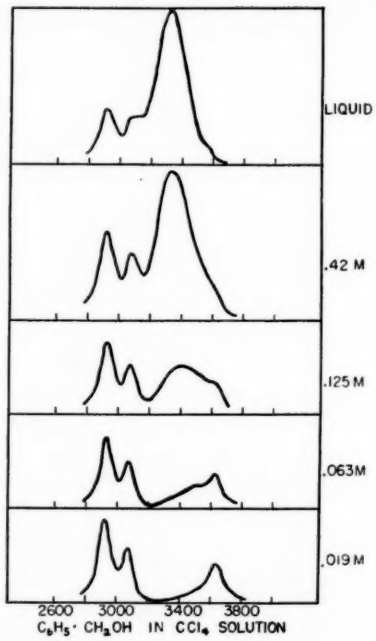

FIG. 5. Absorption curves for benzyl alcohol.

done in order to make the total absorption comparable. The results are shown in Figs. 2, 3, 4 and 5 and are very illuminating. As the concentration is increased, the band at 3700 cm^{-1} is reduced in intensity and an absorption band at 3400 cm^{-1} (2.95μ) appears, with an intensity much greater than the original hydroxyl band. This is presumed to indicate an intermolecular hydrogen bond and is as was observed in our previous note at a slightly higher frequency than in the case of intramolecular bonding. We have not attempted to determine whether the association involves only dimers or higher polymers and we shall postpone the discussion of the nature of the complex formed for the time being.

It may be noted that the first harmonic of the hydroxyl group appears to be absent in the case of the pure liquid alcohols. A small amount of absorption is obtained in the region of this harmonic for liquid water. One may suspect that water is not completely associated at the higher temperatures but that at lower temperatures this harmonic would disappear. If this view is correct, then the well-recognized temperature lability of the hydroxyl group would be identified with the thermal dissociation of hydrogen bonds.

The decreased frequency and increased absorption observed when a hydrogen bond is formed appear to the authors to be a reasonable expectation. With the formation of a hydrogen bond a partial balancing of constraints leaves the hydrogen more free and the dipole moment should possibly be increased. The absence of the harmonic is perhaps not surprising. The energy necessary to excite the first harmonic is a great deal more than is necessary to dissociate the hydrogen bond and a diffuse absorption would easily escape detection.

The authors wish to acknowledge their indebtedness to the Rockefeller Foundation for the financial support which enabled them to undertake this work.

The Surface Tension of Deuterium Oxide and of its Mixtures with Water

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The surface tension, σ, of 97.8 percent deuterium oxide and of five more dilute mixtures with water has been compared with ordinary water by a modification of the capillary rise method. The results show that the relative surface tension is slightly less than that of pure water and is a linear function of the specific gravity. The data may be represented by the equation $\sigma = 1 - 0.00501\Delta s$, where Δs is the increase in specific gravity over ordinary water. By a slight extrapolation the surface tension of pure deuterium oxide at 25°C is estimated to be 0.999,46 of the surface tension of ordinary water at the same temperature.

INTRODUCTION

THE first determination of the surface tension of deuterium oxide was made by Selwood and Frost[1] soon after the discovery of deuterium. They measured the surface tension at 20°C of three specimens of heavy water having a density, d_4^{20}, of 1.0314, 1.0664, and 1.0970 and obtained 71.5, 69.8 and 68.1 dynes per cm, respectively, compared with 72.75 dynes per cm for ordinary water. By extrapolation to a density of 1.1056, which they assumed to be the density of pure deuterium oxide they estimated the surface tension of pure deuterium oxide to be 67.8 dynes per cm, or 6.8 percent less than that of water. Recently Lachs and Minkow[2] have obtained very different results. They made measurements of five specimens ranging from 94 to 99+ percent of deuterium oxide by the use of a DuNouy tensiometer and also by the capillary rise method. These specimens all had the same surface tension as ordinary water within the limit of error of their experiments which was about 1 percent.

The great discrepancy between these earlier results makes it advisable to make new measurements of the surface tension of heavy water by our improved technique on specimens which have been treated so as to ensure the absence of capillary active impurities.

Professor Urey has kindly supplied us with specimens of heavy water ranging from about 22 percent to 97 percent of deuterium oxide for this purpose. These specimens were used for the determination of the viscosity before being used for the measurements of the surface tension.[3]

EXPERIMENTAL

We have recently developed a modification of the capillary rise method of measuring the surface tension of solutions relative to that of pure water which has enabled us to obtain much greater precision than any of the earlier experimenters. In our modification of the capillary rise method[4] the necessity of determining the radius of the capillary tube is entirely eliminated by always bringing the meniscus of the two liquids to be compared to the same fixed reference mark on the capillary tube. That makes it necessary to determine the difference in levels in the wide tube. The serious experimental difficulties in doing this precisely by means of a cathetometer in accordance with the usual practice have been avoided by making the wide tube a right circular cylinder and computing the difference in levels from the weight of the liquids in the instrument and the density which is determined independently. For a more detailed description of the experimental technique and a precision analysis of the method our original paper should be consulted.

It is well known that a trace of grease on water causes a substantial decrease in the surface tension. Preliminary experiments made with ordinary water showed that it is impossible to pass water, either in the liquid or vapor state, through a stopcock which had been lubricated even very

[1] P. W. Selwood and A. A. Frost, J. Am. Chem. Soc. **55**, 4335 (1933).
[2] H. Lachs and I. Minkow, Nature **136**, 186 (1935).
[3] Grinnell Jones and H. J. Fornwalt, J. Chem. Phys. **4**, 30 (1936).
[4] Grinnell Jones and Wendell A. Ray, J. Am. Chem. Soc. **59**, 187 (1937).

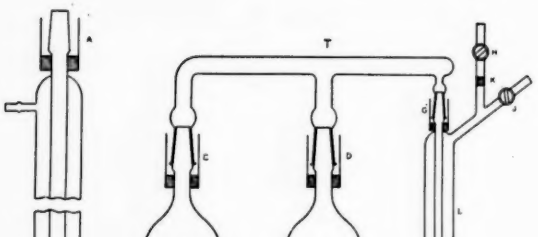

FIG. 1.

slightly with stopcock grease without contaminating the surface of the water enough to cause a serious error in the surface tension. It was also found that the grease could not be completely removed from a contaminated sample of water by three redistillations in a vacuum. Boiling for many hours with a reflux condenser after adding a little sodium hydroxide and potassium permanganate was required to remove every trace of grease. We, therefore, developed a technique for the purification of the samples of heavy water, their transfer to the capillarimeter and pycnometers and the recovery of the heavy water in sealed bulbs with a minimum of exposure to the air and a minimum of loss, and without passing the water through greased ground joints or stopcocks. The various parts of the Pyrex glass apparatus (see Fig. 1) used for the purification and transfer were provided with interchangeable standard taper ground joints. Each joint was provided with an external cup which could be filled with mercury thus making the joints vacuum tight without using any stopcock grease. Since the specimens of heavy water supplied to us by Professor Urey which had been used in this laboratory by Jones and Fornwalt for measurements of viscosity were not quite sufficient to fill our instrument, a small amount of Norwegian heavy water was added after the viscosity measurements were completed. This accounts for the slight difference in density between the specimens used for the viscosity and for the surface tension measurements.

A little solid potassium permanganate and sodium hydroxide were added to each specimen of heavy water and the bulb (E) containing it attached to a reflux condenser (B). The specimen was then heated to boiling and refluxed for at least 12 hours. After cooling the specimen, a tube (T) which served to make a connection to another bulb (F) and to a vapor trap (L) was added to the top of the condenser. Beyond the trap is a tube connected through a stopcock (J) to a vacuum pump (not shown in the diagram) and another tube containing a sintered glass porous plug (K) and a stopcock (H). Then having filled the cups A, C, D and G with mercury and cooled the heavy water in the bulb (E) with ice and cooled the trap (L) by means of solid carbon dioxide and ether, the cock (J) was opened and the system evacuated. The trap serves to prevent any appreciable loss of heavy water during this process. The cock (J) was then closed and the bulb (F) chilled by external application of ice and the bulb (E) and trap (L) warmed gently, thus distilling the water without ebullition into the bulb (F). The cock (H) was then opened, thus admitting air through a drying train (not shown in the diagram) and the porous plug (K). The bulb (E) containing the residue of potassium permanganate and sodium hydroxide and the reflux condenser were then removed and replaced by a clean, dry bulb, and then the system was evacuated as before and the heavy water distilled from (F) into the new (E). The transfer pipet was then attached by means of a suitable adapter in place of the bulb (F) and after evacuation a suitable quantity of heavy water distilled into the transfer pipet. The heavy water was then transferred to the capillarimeter and the measurements carried out as described in our earlier paper, except that no attempt was made to bring the heavy water to any predetermined mark on the capillary and therefore it was not necessary to place any heavy water in the dropping device in the cross head. The actual position of the meniscus of the heavy water in the capillary was observed by the cathetometer, and this served as the reference mark for this experiment. The weight of the capillarimeter and its contents was then determined. The heavy water was transferred in the liquid condition from the capillarimeter to an Ostwald pycnometer of about 50 ml capacity by

the use of a suitable adapter and the specific gravity determined. The heavy water from the pycnometer and the small amounts wetting the walls of the capillarimeter, transfer pipets and adapters were then recovered for storage in suitable bulbs by the vacuum distillation technique.

In the calibration with ordinary water the dropping device in the cross head (see Fig. 1 of our earlier paper) was used to bring the meniscus to the same reference mark which had been selected in the previous experiment with heavy water.

Discussion of Results

The deuterium oxide-water mixtures whose surface tension we have measured are best defined in terms of the specific gravity in vacuum at 25°C as shown in the first column of Table I. The specific gravity, d_{25}^{25}, characterizes the sample definitely, except for a slight ambiguity as to the relative amounts of the isotopes of oxygen which are present. The mole fraction of deuterium oxide, given in the second column, is computed from the specific gravity by the equation:[3]

$$N=0.0002+9.375\Delta s-1.03(\Delta s)^2+0.2(\Delta s)^3,$$

where $\Delta s=d_{25}^{25}-1$. The third column of the table gives the surface tension of the deuterium oxide-water mixtures relative to that of pure water at 25°C as determined experimentally by the method and apparatus described in detail in our earlier paper. This relative surface tension has been determined with greater precision than the absolute surface tension of water is known.

The surface tension is a linear function of the specific gravity as is shown by the plot of the data in Fig. 2. The experimental results are represented by the equation $\sigma=1-0.00501\Delta s$ within the limit of error of the data. The deviations between the experimental data and the results computed by this equation are shown in the last column of the table. The maximum deviation of any result is only 0.004 percent and the average deviation is only 0.0013 percent.

Table I. *The surface tension of deuterium oxide-water mixtures at 25°C relative to that of pure water at 25°C.*

d_{25}^{25}	N	σ obs.	σ obs. $-\sigma$ comp.
1.000,607	0.0059	1.000,00	0.000,00
1.024,114	0.2257	0.999,92	+0.000,04
1.058,210	0.5424	0.999,73	+0.000,02
1.075,873	0.7057	0.999,62	0.000,00
1.089,171	0.8281	0.999,53	−0.000,02
1.105,266	0.9759	0.999,47	0.000,00
(1.107,9)	1.000	(0.999,46)	extrapolated

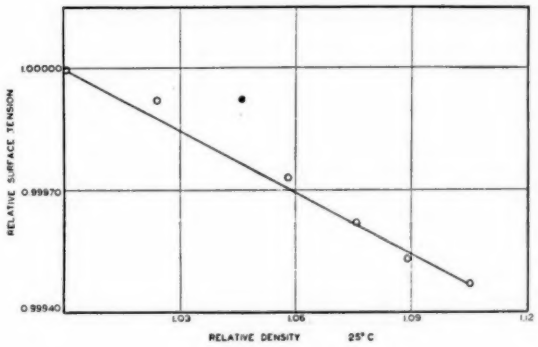

Fig. 2.

This equation may be used to compute the surface tension of pure deuterium oxide by a short extrapolation. According to Selwood, Taylor, Hipple and Bleakney[5] the specific gravity of pure deuterium oxide, d_{25}^{25}, is 1.10790; and according to Tronstad, Nordhagen and Brun,[6] d_{25}^{25} is 1.1074. Either of these values leads to the value 0.999,46 for the relative surface tension of pure deuterium oxide at 25°C. Although the difference between deuterium oxide and water is slight we believe that it is a real difference and not due to experimental error. The large difference found by Selwood and Frost is not confirmed. It seems probable that their specimens contained traces of capillary active impurities. Our results agree with those of Lachs and Minkow within their limit of error.

It is of interest to contrast the approximate equality of the surface tension of deuterium oxide and of water with the difference in viscosity of twenty-three percent found by Jones and Fornwalt. The viscosity depends on the transfer of kinetic energy by molecular collisions across planes of shear during flow. In this process the mass plays an important role. On the other hand, the surface tension depends primarily on the mutual attraction between molecules at rest

[5] P. W. Selwood, H. S. Taylor, J. A. Hipple, Jr. and W. Bleakney, J. Am. Chem. Soc. **57**, 642 (1935).
[6] L. Tronstad, J. Nordhagen and J. Brun, Nature **136**, 515 (1935).

which depends largely, if not wholly, on the properties of the molecules as electric dipoles. This electric force depends on the charge and on the separation of the dipoles, and would be expected to be independent of the mass. Since the molecular volume of deuterium oxide is slightly greater than that of water the slight decrease in surface tension which is found experimentally may be ascribed to the greater separation of the dipoles. The facts may therefore be accounted for without ascribing any direct influence of the mass on the surface tension.

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Raman Spectra of Amino Acids and Related Compounds

IV. Ionization of Di- and Tricarboxylic Acids

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A systematic study of Raman spectra has been made for a large number of carboxylic acids and their salts dissolved in water. In particular, malonic acid and its two sodium salts, and malonic-d_2 acid-d_2 and its disodium salt, have been studied in detail. The substitution of deuterium in this molecule permits the vibrations arising primarily from the $-CH_2$ group to be distinguished from those arising primarily from the carboxyl groups. The Raman spectrum of deuterium oxide has been redetermined in connection with these studies. The following general conclusions have been reached: (1) The powerful "carbonyl" frequency near 1700 cm^{-1} is always found when an un-ionized carboxyl group is present, and always vanishes on ionization of the carboxyl. (2) One or more intense Raman lines near 1400 cm^{-1} can always be found in a substance containing an ionized carboxyl group. Such lines are definitely polarized, and presumably correspond to a symmetrical valence oscillation of the COO^- group. Like the "C=O" frequency near 1700, these lines are almost unaffected by deuterium substitution. Deformation frequencies arising from $-CH_2$ or $-CH_3$ groups commonly lie in the same range; the marked effect of deuterium substitution, however, clearly differentiates these from the vibrations of the $-COO^-$ group. (3) Other Raman lines, near 1330 and 1580 cm^{-1}, are frequently but not invariably found in substances containing ionized carboxyl groups. (4) Most of the substances studied show strong Raman lines between 700 and 950 cm^{-1}, which increase in frequency by 30 to 50 cm^{-1} on ionization. These lines are strongly polarized, and in malonic acid are noticeably depressed in frequency by deuterium substitution. (5) Certain frequencies below 600 cm^{-1} are virtually unaffected either by ionization or by deuterium substitution. These presumably represent bending or twisting vibrations of the heavy molecular framework. The "C=C" frequency near 1650 in crotonic and maleic acids is unchanged by the ionization of a neighboring carboxyl group. The Raman spectra of *d*-tartaric acid and of mesotartaric acid, although very similar, show definite differences which are well beyond the experimental error. The structure of the ionized carboxyl group is undoubtedly closely related to that of the nitro group. Both show intense polarized Raman lines near 1400, probably corresponding to the same type of oscillation in both cases; and the bond strength in the two groups is probably nearly the same.

INTRODUCTION

A SYSTEMATIC study of the effect of ionization of the carboxyl group on the Raman spectrum of fatty acids and amino acids has already been begun.[1] This study has now been extended to a considerable number of acids containing two or three carboxyl groups. Malonic acid has been studied with particular attention, the effect of ionization and also of deuterium substitution having been examined in detail. The large number of carboxylic acids which has now been studied permits certain definite generalizations concerning the effect of ionization, and furnishes a basis for an analysis of the structure of the carboxyl group.

EXPERIMENTAL

The methods used were essentially the same as those described in the previous studies of this series.[2, 3] It may be noted, however, that, in studying the salts of the acids, it is important to maintain the solution slightly acid to neutrality

[1] J. T. Edsall, J. Chem. Phys. **4**, 1 (1936).

[2] J. T. Edsall, J. Phys. Chem. **41**, 133 (1937).
[3] J. T. Edsall, J. Chem. Phys. **5**, 225 (1937).

or, in any case, not more alkaline than *p*H 8. In solutions more alkaline, the Norit used as a clarifying agent in filtration gives off a fluorescent impurity which renders it almost impossible to obtain clear Raman spectra. The acidity of the solutions, therefore, was always tested by means of a suitable indicator before filtration was carried out.

Malonic-d_2 acid-d_2 was prepared by treating malonic acid (m.p. 134–135°) with 99.5 percent D_2O, evaporating off the heavy water after a few hours' standing, repeating the process, again dissolving the acid in D_2O and filtering directly into the Raman tube. Halford and Anderson[4] have shown that all the hydrogens in malonic acid are readily replaced by deuterium under these circumstances, and the Raman spectra entirely confirm their conclusion, since the C−H frequencies above 2900 cm^{-1} had quite disappeared from the spectrum after this treatment.

Disodium malonate-d_2 was similarly prepared from disodium malonate (a sample previously

[4] J. O. Halford and L. C. Anderson, J. Am. Chem. Soc. **58**, 736 (1936).

TABLE II. *Characteristic frequencies of the CH_2 and CD_2 groups in the malonic acids.*

	$-CH_2$	$-CD_2$	RATIO
ν_1	2956(6)	2159(5)	1.368
ν_2	3003(3)	2258(3)	1.332
δ	1417(4*b*)	1050(4)	1.349

TABLE I. *Raman spectra of malonic acid, malonic-d_2 acid-d_2, and the ions derived from them.*

1	2	3	4	5	
H, COOH, C, H, COOH	H, COOH, C, H, COO^-	H, COO^-, C, H, COO^-	D, COOD, C, D, COOD	D, COO^-, C, D, COO^-	
427(4*b*)	434(5)	427(3*b*)	412(3)	414(1*b*)	*A*
590(2*b*)	586(2*b*)	590(3*b*)	538($\frac{1}{2}b$)	573±35(1*b*)	*B*
660(2*b*)	664(3*b*)	698(1*b*)	607(1)	654($\frac{1}{2}$)	*C*
773(4*b*)	802(2*b*)	828(3*b*)	733(3) 790($\frac{1}{2}$)	810(2)	*D*
919(8*b*)	923(8*vb*)	935(6) 956(3)	845(3)	873(3) 910(2)	*E*
1031(0*b*)			940(0)	940(1)	*F*
1181(2*b*)	1193(1*vb*)	1181(3)	1106($\frac{1}{2}$)	1106(1)	*G*
1308(0)	1278($\frac{1}{2}$)	1260(2*b*)	1360(1)		*H*
	1372(5)	1361(6)		1367(4)	*I*
1417(4*b*)	1408(5*b*)	1413(6)	1050(4)	1054(4)	*J*
		1439(6)		1427(7)	*K*
		1587(1*vb*)		1573(2*b*)	*L*
	1639(0*vb*)[H_2O?]		1209($\frac{1}{2}b$)[D_2O?]	1228($\frac{1}{2}vb$)[D_2O?]	*M*
1738(8*b*)	1730(2*b*)		1719(7*b*)		*N*
2956(6)	2943(6)	2947(6*b*)	2159(5)	2153(5)	*O*
3003(3)	2987(1)	2984(2*b*)	2258(3)	2238(3)	*P*

The frequencies in the row marked *M* probably arise from the solvent. Observations on deuterium oxide gave the spectrum: 1209±20 (1/2)(*K*, *e*); 1383 (0)(*e*?); 2370 (8)(*K*, *e*); 2517 (12)(*K*, *e*); 2679 (4)(*K*?). The doubtful line at 1383 (due possibly to HDO?) has not been reported by others. Compare R. Ananthakrishnan, Proc. Indian Acad. Sci. **A2**, 291 (1935); **3**, 201 (1936) and E. Bauer and M. Magat, Comptes rendus **201**, 667 (1935). The very faint Raman bands near 350 and 500 cm^{-1}, reported by the latter authors, are clearly too weak and broad to disturb the observation of the malonic acid spectrum.

TABLE III. *Raman frequencies shifted by ionization in the range 700–1000 cm⁻¹.*

SUBSTANCE	UN-IONIZED ACID	COMPLETELY IONIZED ACID
Crotonic Acid	690(2*b*)	730(2*b*)
Glycolic Acid	898(6)	932(6)
Oxalic Acid	852(6)	902(6)
Malonic Acid	773(4)	828(3*b*)
	919(8*b*)	935(6); 956(3)
Malonic-d_2 Acid-d_2	733(3)	810(2*b*)
	845(3)	873(3*b*); 910(2*b*)
Succinic Acid	837(6)	873(6)
	935(2)	957(6)
d-Tartaric Acid	754(6)	805(4)
l-Aspartic Acid	822(4)	858(4)
d-Glutamic Acid	917(2)	937(4*b*)
Maleic Acid	869(6)	903(4)
Tricarballylic Acid	930(4)	948(5*b*)
Citric Acid	800(5)	845(4)
	939(6)	956(5)

The data for glycolic and succinic acids are taken from I. Pèyches, Bull. Soc. Chim. [5] 2, 2195 (1935).

employed for determination of Raman spectrum) and D_2O.

DISCUSSION

The malonic acids

The study of malonic acid, malonic-d_2 acid-d_2, and the ions derived from them, reveals particularly clearly the types of Raman frequencies encountered in carboxylic acids and their salts. The data are set forth in Table I, frequencies which appear to correspond being placed in the same row. (In a few cases, as in the rows marked *F* and *H*, it is dubious whether the frequencies grouped together actually correspond.) Several criteria have been employed in establishing such correspondence: relative intensity of the lines, relative polarization (in the case of malonic acid

TABLE IV. *Effect of ionization on frequencies in the range 1300 to 1750 cm⁻¹.*

		(1)	(2)	(3)	(4)	(5)
1. Oxalic Acid	$R\cdot(COOH)_2^-$	1310(0)	1460($\frac{1}{2}$)		1645(2)	1750(3)
	$R\cdot(COO)_2^{--}$	1311(4)	*1457(4) *1489(7)		*1580(1*b*) 1647(2*vb*)	
2. Malonic Acid	$R\cdot(COOH)_2$		1417(4*b*)			1738(8*vb*)
	$R\cdot COOH\cdot(COO)^-$	*1372(5)	1408(5*b*)			1730(2*b*)
	$R\cdot(COO)_2^{--}$	*1361(6)	1413(6)	*1439(6)	*1587(1*vb*)	
3. Malonic-d_2 Acid-d_2	$R\cdot(COOD)_2$	1360(1)				1719(7*b*)
	$R\cdot(COO)_2^{--}$	*1367(4*b*)		*1427(7)	*1573(2*b*)	
4. Succinic Acid	$R\cdot(COOH)_2$	1339(0)	1409(3)		1637(3*b*)	1702(3)
	$R\cdot(COO)_2^{--}$	*1330(3)	*1410(6)		*1555(3*b*) 1640(3*b*)	
5. Crotonic Acid	$R\cdot COOH$	1302(6)	1383(3)	1451(4)	1658(5)	1700(2)
	$R\cdot COO^-$	1297(5)	*1396(4*vb*)	1450(4)	1661(7*b*)	
6. Maleic Acid	$R\cdot(COOH)_2$	1325(1*b*)	1390(1*vb*)		1654(6*b*)	1725(6*vb*)
	$R\cdot(COO)_2^{--}$	1306(2)	*1400(6) *1434(2)		*1570(1*vb*) 1647(6)	
7. *d*-Tartaric Acid	$R\cdot(COOH)_2$		1413(1)	1442(2)		1740(5*b*)
	$R\cdot(COO)_2^{---}$	*1310(2*b*) *1370(5*b*)	*1418(6*b*)		*1617(1*vb*)	
8. *l*-Aspartic Acid	$R\cdot(COOH)_2$	1376($\frac{1}{2}$)	1418(1)		1634($\frac{1}{2}$)	1743(4*vb*)
	$R\cdot(COO)_2^{--}$	*1330(1) *1355(2)	*1411(5*b*)		1620±50(1*vb*)	
9. *d*-Glutamic Acid	$R\cdot(COOH)_2$	1347($\frac{1}{2}$)	1433(3)		1649($\frac{1}{2}$*vb*)	1736(4*vb*)
	$R\cdot(COO)_2^{--}$	*1345(2*b*)	*1410(4*b*)		*1625(2*vb*)	

and disodium malonate), similarity in the effects of ionization for the hydrogen and deuterium compounds. Furthermore, the studies of Angus, Leckie and Wilson[5] and of Engler[6] on CH_3COOH, CH_3COOD and CD_3COOD furnish a very valuable set of comparative data for testing the reasonableness of the assignments made. Thus the lines 1359 and 1436 in CH_3COOH go over into 1025 and 1093, respectively, in CD_3COOD. Likewise, the line at 1417 in $CH_2(COOH)_2$ goes over into 1050 in $CD_2(COOD)_2$.

Apart from the frequency marked *M*, which probably arises from the solvent, only three Raman lines are shifted as much as ten percent by deuterium substitution. These three (*J*, *O* and *P* in Table I) are shifted by more than thirty percent. Hence they must arise primarily from the $-CH_2$ or $-CD_2$ group. Such a group, considered as a separate entity (a "pseudo-triatomic molecule") should give rise to three fundamental frequencies: two valence oscillations (ν_1 and ν_2) and one symmetrical deformation (δ) (Table II).[7] Although polarization measurements have not been carried out on ν_1 and ν_2, it is

[5] W. R. Angus, A. H. Leckie and C. L. Wilson, Proc. Roy. Soc. **A, 155**, 183 (1936).
[6] Engler, Zeits. f. physik. Chemie **B32**, 471 (1936).

[7] Other modes of vibration in these molecules undoubtedly exist, in which the hydrogens of the CH_2 or CD_2 groups play an important part (for instance, a bending frequency involving a motion of the hydrogens approximately parallel to the plane of the three carbon atoms). Such frequencies, however, if they do give rise to any of the observed Raman lines, are much less affected by deuterium substitution than the three listed in Table II. Raman lines arising from the carboxylic O−H and O−D groups might be expected to appear, but have not been found. Quite probably they coincide with the intense bands arising from the solvent H_2O or D_2O.

TABLE IV.—*Continued.*

		(1)	(2)	(3)	(4)	(5)
10. Tricarballylic Acid	$R\cdot(COOH)_3$		1420(5*b*)			1724(6*b*)
	$R\cdot(COO)_3^{---}$	*1333(3*b*)	*1419(8*b*)		*1571(1*b*)	
11. Citric Acid	$R\cdot(COOH)_3$		1403(3)	1438(2)		1731(6*b*)
	$R\cdot(COO)_3^{---}$	*1302(0)	*1415(8*b*)		*1580($\frac{1}{2}$*b*)	
12. Lactic Acid	$R\cdot COOH$	1381(1)	1446(3)			1710(3)
	$R\cdot COO^-$	1380(1)	*1411(5)		*1605−30(3)	
13. Glycolic Acid	$R\cdot COOH$	1372(1*b*)	1449(5)			1733(5*b*)
	$R\cdot COO^-$	1355(2*b*)	*1434(5*b*)		*1596(3*b*) 1632(3*b*)	
14. Sarcosine	$R\cdot COOH$	1284(1)	1429(2)	1464(3)	1622($\frac{1}{2}$*vb*)	1732(1*b*)
	$R\cdot COO^-$	*1320(3*b*)	*1408(5*b*)	1468(4)	1633(2*vb*)	
15. Betaine	$R\cdot COOH$	1337($\frac{1}{2}$)	1419($\frac{1}{2}$)	1453(4)		1751(1*b*)
	$R\cdot COO^-$	*1335(2)	*1403(2)	1453(2)	1638(0*b*)	
16. Di-Methyl Phenyl Betaine	$R\cdot COOH$	1327(0*b*)		1468(3*b*)		1750(0*vb*)
	$R\cdot COO^-$	*1330(3*b*)	*1404(3*b*)	1465(3*b*)		
17. β-Alanine	$R\cdot COOH$	1328(2*b*)	1413(3*b*)	1472(1*b*)	1630(1*vb*)	1730(4*b*)
	$R\cdot COO^-$	1338(1)	*1410(5*b*)	1471($\frac{1}{2}$)	1630(1*vb*)	
18. β-Amino-*n*-Butyric Acid	$R\cdot COOH$	1380(2*b*)	1419(2)	1461(4)	1637(2*vb*)	1726(4*vb*)
	$R\cdot COO^-$	1366($\frac{1}{2}$)	*1408(7*b*)	1457(3)	1641(1*vb*)	

The data for succinic, glycolic and lactic acids and their salts are taken from I. Peychès (Bull. Soc. Chim. (5) **2**, 2195 (1935)), who has also studied *d*-tartaric acid and its salts in detail; the data here presented on tartaric acid and the tartrates are in close accord with those of Peychès. The complete Raman spectra of the substances numbered 14–18, inclusive, will be published later.
This table may be regarded as a continuation of Table I in reference 1, except that the grouping of frequencies into columns is somewhat different. Lines marked * appear to be closely associated with the ionized carboxyl group. Lines near 1630, listed in column 4, may arise largely from the water used as solvent.

probable that the more intense line (ν_1) represents a symmetric, and the weaker (ν_2) an antisymmetric, valence vibration. Angus, Leckie and Wilson[5] have suggested that the ratio of corresponding frequencies for the $-CH_3$ and $-CD_3$ groups should roughly be equal to the reciprocal of the square root of the ratio of the reduced masses of the C−H and C−D atomic pairs, or 1.36. Although this conception is undoubtedly over-simplified, it does give a fair approximation to the facts for the $-CH_2$ and $-CD_2$ groups (see Table II).[8]

We may now consider the other Raman lines in Table I. The lowest frequency (*A*) is unaffected by ionization and almost unaffected by deuterium substitution; its depolarization factor is high. It probably corresponds to an asymmetrical bending or twisting of the heavy framework of the molecule. The line *B* is strongly polarized, and may arise from a symmetrical deformation, which probably largely involves the carboxyl groups. The lines *D* and *E* are also strongly polarized; they are markedly increased in frequency by ionization, and depressed by deuterium substitution. In this they are very similar to the strong line at 895 in acetic acid, which is highly polarized, which increases in frequency to 928 on ionization[1] and falls to 800 in CD_3COOD.[5, 6] A great number of other carboxylic acids (see reference 1, and Table III of this paper) show Raman lines of apparently similar nature. Their character is further discussed below, in connection with Table III.

The lines *I*, *K*, *L* and *N* evidently arise from the carboxyl group. Whether they appear or not depends on the state of ionization of this group; deuterium substitution affects them very little. Thus the very intense and polarized line at 1738 in $CH_2(COOH)_2$ (the "C=O frequency") is decreased only to 1719 in $CD_2(COOD)_2$.[9] On the other hand, ionization of one carboxyl group greatly weakens its intensity (although scarcely diminishing the frequency) and ionization of both carboxyl groups abolishes it altogether. This behavior is typical of all carboxylic acids hitherto investigated (see Table IV).

[8] Another very weak frequency near 2075 was found in malonic-d_2 acid-d_2 and its disodium salt (see Table V).

[9] Similarly the "C=O frequency" which lies near 1670 in CH_3COOH, decreases only to 1657 in CD_3COOD (reference 5).

The lines *I*, *K* and *L*, on the other hand, arise primarily from the *ionized* carboxyl group. The line near 1370 appears at the first step in ionization; those near 1430 and 1580 at the second. The 1430 line is strongly polarized; the other two less markedly so.

The lines near 1400 happen to coincide very nearly with the deformation frequencies of the $-CH_2$ and $-CH_3$ groups. The effect of deuterium substitution, however, clearly differentiates the two types of vibration. In disodium malonate, the three lines 1361, 1413, and 1439 are almost equally intense. In disodium malonate-d_2, 1413 is completely gone, its place being taken by 1054; while the other two lines are virtually unchanged, and must, therefore, be associated primarily with the ionized carboxyl group.

Raman Lines of Other Carboxylic Acids and Their Salts

Most of the characteristic features of the spectra of the malonic acids and their salts are also found in the other acids studied. Most of the molecules studied possess one or more Raman frequencies in the region below 600 cm^{-1}, which remain essentially unaffected by ionization, like the lines at 430 and 590 in malonic acid (see Table V). These presumably correspond to deformations of the molecular framework.

The "sensitive frequency" between 700 and 1000 cm^{-1}

In this region, practically all the acids studied show one or two powerful Raman lines which are increased in frequency by 20 to 50 cm^{-1} on ionization of the carboxyl group (Table III). Exactly similar lines have already been reported in several fatty acids and amino acids (reference 1, Table II). Where polarization measurements have been made (as in acetic and malonic acids, and dipotassium oxalate) these lines have all been found to be very strongly polarized. They fall in the same frequency range as the totally symmetric vibrations of the methylated methanes[10] and ammonium ions;[3] and in all cases this type of frequency is depressed by the replacement of hydrogen by a methyl group on

[10] K. W. F. Kohlrausch and F. Koppl, Zeits. f. physik. Chemie **B26**, 209 (1934).

the central carbon atom.[1] Probably then this type of vibration in the carboxylic acids is similar to that found in the other compounds mentioned, being of course modified in detail by the presence of the carboxyl group. The increase in the frequency on ionization, and the decrease on deuterium substitution, suggest that the change of mass involved in both cases is primarily responsible for the shift. Thus for acetic acid[1, 5] we have the series:

CH_3COO^-	CH_3COOH	CH_3COOD	CD_3COOD
928 cm^{-1}	898	850	800

In this case, certainly, increase in mass of the vibrating groups is directly correlated with the decrease in frequency (for the malonic acids, see rows *D* and *E* in Table I).

d-Tartaric acid and mesotartaric acid

These isomers (Table V no. 13 and 15) have very similar Raman spectra, as might be expected, but the differences between them are well beyond the magnitude of the experimental error. Particularly is this true for the frequencies in the region 700–1100 cm^{-1}, where the mutual orientation of the $-OH$ and $-COOH$ groups evidently induces significant differences. A further study of some optically active and meso isomers will be undertaken later.

Raman lines between 1300 and 1750 cm^{-1}

We may now consider the frequencies in this range (arising probably for the most part from the C–H linkages and the carboxylic group). The data available are given in Table IV, which is essentially a continuation of data previously reported (see reference 1, Table I).

The "carbonyl" frequency, between 1700 and 1750 cm^{-1}, (Table IV, column 5) is found invariably in un-ionized carboxylic acids, and invariably vanishes on complete ionization of the carboxyl group. No exception to this rule has been found among the twenty-six carboxylic acids tabulated in this and the previous investigation.[1] For a saturated fatty acid, dissolved in water,[1] this frequency is very near 1720 cm^{-1}. Crotonic acid shows a lower value of 1700; this depressing effect of an adjoining double bond on the carbonyl frequency is well known for other compounds.[11] The C=O frequency in lactic acid is also rather low; in all the other compounds reported, however, it is higher than in the fatty acids. The influence of an adjoining carboxyl group, like that of a charged $-NH_3^+$ group, is thus to increase the C=O frequency.

The presence of one or more strong frequencies near 1400 cm^{-1} is apparently characteristic of the *ionized* carboxyl group. In the case of the malonic acids, already discussed, this fact stands forth with particular clarity. In many other carboxylic acids, these frequencies are less easily recognized, because of the presence of other lines in the same region of the spectrum, arising from different modes of vibration (commonly from $-CH_2$ and $-CH_3$ groups). The effect of ionization, however, is always shown by a great increase of intensity (and often a shift of frequency) of one or more lines near 1400 cm^{-1} (see Table IV, column 2, lines marked *, also some of the lines listed in columns 1 and 3). In the formate, malonate and oxalate ions, these lines are strongly polarized, and must correspond to a symmetrical oscillation. Probably the same is true for the other ionized carboxylic acids.

A typical example of the effect of ionization is shown in Fig. 1. Maleic acid in solution shows the two adjoining powerful frequencies, 1654 and 1725. There is only one faint line near 1400 (not clearly visible on the microphotometer tracing). In disodium maleate, the 1650 line is virtually unchanged in frequency or intensity, but the 1725 line has vanished, being replaced by a very powerful line at 1400, with a weaker satelite at 1434. In Fig. 2 (crotonic acid and sodium crotonate) the effect of ionization is also unmistakable, although less obvious. The free acid shows three strong lines at 1302, 1383 and 1451. On ionization of the carboxyl group, the first and third appear essentially unchanged, but the middle line—formerly the weakest of the three—becomes much broader and decidedly more

[11] A. Dadieu, A. Pongratz and K. W. F. Kohlrausch, Ber. Wiener Akad. Wiss IIa, **140**, 353, 647 (1931) studied the Raman spectrum of pure crotonic acid above its melting point and found one frequency in this range at 1654, while we obtain two frequencies (1658 and 1700) in the aqueous solution. In pure liquid fatty acids, the C=O frequency is about 50 cm^{-1} lower than in their aqueous solutions (reference 1). Similarly the C=O frequency in pure crotonic acid should lie near 1650, where it will coincide with the "C=C" frequency and not be observed. This probably explains the difference between Kohlrausch's observations and ours.

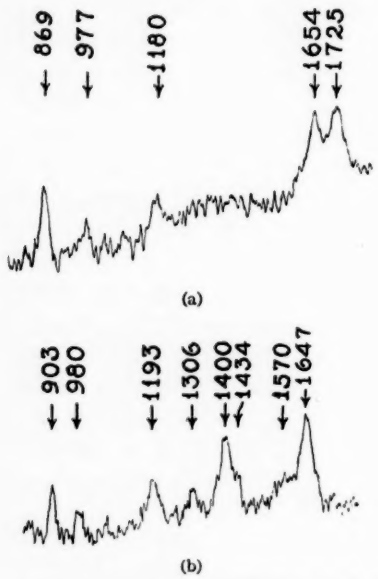


FIG. 1. Microphotometer tracings of Raman spectra of (a) maleic acid and (b) disodium maleate in water in the region 800–1750 cm^{-1}. These spectra were excited by Hg 4358A.

intense, its maximum also being displaced to 1396.

Such changes as this are typical of all carboxylic acids investigated. Acetic acid,[1] for instance, gives a fairly strong and depolarized line at 1430, which as the effect of deuterium substitution shows,[5] arises from the methyl group. Sodium acetate shows a rather similar line at 1413, which was formerly attributed to the same origin.[1] The latter line, however, is very much more intense than that in the free acid: probably it represents two different frequencies which accidentally coincide—one arising from the methyl and one from the carboxyl group. The latter component should be definitely polarized (in contradistinction to the 1430 line in acetic acid), and in sodium acetate-d_3 it should remain nearly unchanged while the component arising from the methyl group should be shifted to a value near 1100.[12]

A frequency near 1400 is thus apparently as characteristic of the ionized carboxyl group as the frequency near 1700 is of the same group when un-ionized. In the formate ion, this frequency has the unusually low value 1351; in the oxalate ion, it corresponds to the doublet, 1457 and 1489; in the malonate ion to the doublet, 1370 and 1439. In most of the other substances studied this frequency lies at 1405 ± 10.[13]

In many, but not all, of the substances studied, a strong line near 1340 makes its appearance on ionization of the carboxyl group (Table IV, column 1). Another line near 1580 (column 4) is also frequently found under the same circumstances. The fact that this line appears with almost identical frequency in disodium malonate and in disodium malonate-d_2 indicates its probable association with the ionized carboxyl group. Polarization measurements on dipotassium oxalate and disodium malonate solutions indicate that this line has a high depolarization factor (nearly, if not quite, 6/7).

The structure of the carboxyl group

It is well known that the "carbonyl" frequency near 1700 cm^{-1} is nearly independent of the length of the attached hydrocarbon chain;[13] likewise, both in acetic acid[5, 6] and in acetone,[6] it is almost unaffected by the substitution of deuterium for hydrogen in adjoining groups of the molecule. It appears probable, then, that this frequency really does correspond to a normal

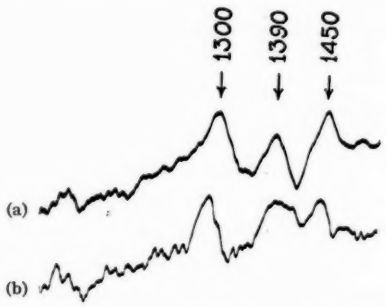


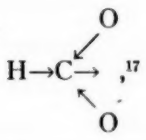
FIG. 2. Raman spectrum of (a) crotonic acid (b) sodium crotonate, in the region 1200–1450 cm^{-1}, excited by Hg 4047A. Note the increase in breadth and intensity of the line near 1390 in sodium crotonate as compared with crotonic acid.

[12] In addition to the data given in Table IV, J. C. Ghosh and B. C. Kar, J. Phys. Chem. **35**, 1735 (1931) have reported a very strong Raman line at 1402 in sodium benzoate, although benzoic acid shows no frequency in this range. This line also may therefore be attributed to the ionized carboxyl group.

[13] K. W. F. Kohlrausch, F. Köppl and A. Pongratz, Zeits. f. physik. Chemie **B21**, 242 (1933) and **22**, 359 (1933) have concluded that a frequency near 1410 is characteristic of the *un-ionized* carboxyl group in the fatty acids. This frequency is much weaker than the 1400 line arising from the ionized group; its polarization character is not yet known. Whether both frequencies arise from a fundamentally similar mode of vibration is a question that cannot yet be answered.

mode of vibration which is essentially an oscillation of the C=O bond; other parts of the molecule undergoing little displacement relative to one another. The recent x-ray studies of Robertson and Woodward[14] on oxalic acid dihydrate show a definite difference in the two C−O bonds of the un-ionized carboxyl group. The longer bond (1.30A) is presumably that to which the hydrogen is attached; the shorter one (1.24A) is undoubtedly the stronger, and corresponds to the C=O linkage of the classical formula. It is presumably the vibration of this latter linkage which gives rise to the "carbonyl" frequency.

The ionized carboxyl group, as might be expected because of resonance, shows a much nearer approach to complete equivalence of the two C−O bonds[15] which probably do not differ in length by more than 0.02A. Thus the COO^- group is closely similar to a bent symmetric triatomic molecule. In electronic structure, it is very intimately related to the nitro group. The latter is found to possess two very characteristic Raman frequencies: one near 1380, which is very intense and polarized, the other near 1560, less intense and depolarized.[16] The intense polarized frequency near 1400, which we have found to be characteristic of the ionized carboxyl group, is thus probably analogous to the 1380 frequency of the nitro group. In the formate ion, the simplest carboxylate ion[1, 2] this frequency (1351 cm^{-1}) presumably corresponds to the normal mode of vibration



which is essentially a symmetrical valence vibration of the COO^- group.[18] In the more complex substances studied, a similar mode of oscillation in the COO^- groups is almost certainly involved.

The asymmetrical valence vibration, which should also be characteristic of the ionized carboxyl group, is less easy to identify. By analogy with the nitro group, it might be identified with the moderately intense line near 1580 (Table IV) found in many, but not all of the ionized carboxylic acids. This line has a high depolarization ratio, as would be expected for such a frequency, but since it has not been found in all the substances studied, final interpretation of its nature must be postponed.

Such a triatomic group as the COO^- group should also give rise to a third, symmetrical deformation frequency, much lower than either of the other two. No such frequency has yet been definitely identified; it might correspond to the polarized line at 590 in the malonate ion, and to similar lines in other compounds studied. Here again interpretation must be postponed.

One very definite point emerges, however, from the comparison of the nitro and the ionized carboxyl group. The masses of the atoms in the two groups are very similar; the principal symmetrical frequencies near 1400 are nearly identical. Hence the force constants of the bonds in the two groups must be nearly alike. They approach values characteristic of double rather than single bonds.[19] On this point the evidence from Raman spectra is entirely consistent with the x-ray diffraction data, and with the relations which have been found to hold between bond character and interatomic distance[20] in these and other groups.

I am indebted to Mr. Joseph Shack for valuable aid in the measurement and tabulation of spectra and to Dr. James H. Hibben for the microphotometer tracings reproduced in Figs. 1 and 2.

[14] J. M. Robertson and I. Woodward, J. Chem. Soc. 1817 (1936).

[15] S. B. Hendricks and M. E. Jefferson, J. Chem. Phys. **4**, 102 (1936).

[16] J. Cabannes and A. Rousset, Ann. de physique **19**, 269 (1933).

[17] See G. B. B. M. Sutherland and D. M. Dennison, Proc. Roy. Soc. **A148**, 250 (1935) for the normal modes of vibration of a molecule of this type (formaldehyde). The vibration shown above is ν_1 in their notation.

[18] This interpretation of the 1351 line in the formate ion has already been proposed by J. Gupta, Indian J. Phys. **10**, 313 (1936), who has found the line to be highly polarized ($\rho=0.16$). Gupta has also (Indian J. Phys. **10**, 199, 465 (1936)) attempted an interpretation of the spectrum of the oxalate ion, whose structure is closely related to that of ethylene. He attributes the intense doublet near 1470 in this ion to what is essentially a symmetrical valence oscillation of the two COO^- groups, in agreement with the view adopted here.

[19] A group of three similar masses held together by single bonds has a much lower characteristic frequency for this type of symmetric oscillation. Thus the value for propane is 867, and for dimethyl amine, 931 (3).

[20] L. Pauling, L. O. Brockway and J. Y. Beach, J. Am. Chem. Soc. **57**, 2705 (1935).

TABLE V. *Complete list of observed Raman spectra.*

The notation used in recording these spectra is the same previously employed.[1-3]

A number of the substances here studied have been previously observed. Detailed studies have been made of *d*-tartaric acid and its salts (footnote, Table III), of oxalic acid[21, 13] and of dipotassium oxalate[18] in water, of crotonic acid in the pure molten state,[11] and of citric acid[23] in water. Other more fragmentary data have been obtained for malonic acid, disodium malonate, disodium maleate and disodium fumarate.[22] The agreement of our own with the earlier data is in general very satisfactory.

1. *Oxalic acid*, HOOC·COOH. 8 percent solution in water. $\Delta\nu$: 464 (3*b*) (*k*, *e*); 852 (6) (*k*, *e*); 1395 (00*b*) (*k* ?); 1476 ($\frac{1}{2}$*b*) (*k*, *e*); 1652±35 (2*vb*) (*e*); 1753 (6*b*) (*e*).

2. *Dipotassium oxalate*, $K^+ {}^-OOC\cdot COO^- K^+$. 25 percent solution in water (prepared from Merck's reagent oxalic acid and two equivalents of concentrated c.p. KOH). $\Delta\nu$: 317 (2) (*e*); 456 (3) (*k*, *e*); 902 (6) (*k*, *e*); 1311 (4) (*k*, *e*); 1457 (4) (*k*, *e*); 1489 (7) (*k*, *e*); 1580 (1*b*) (*e*); 1647 ($\frac{1}{2}$*b*) (*e*).

3. *Malonic acid*, HOOC·CH_2·COOH (Eastman) 40 percent solution in water, +0.4 *N* HCl. $\Delta\nu$: 427 (4*b*) (*k*, ±*e*); 590 (2*b*) (*e*); 660 (2*b*) (*k*, *e*); 773 (4*b*) (*k*, *i*, *e*); 919 (8*b*) (*k*, *i*, *e*); 1031 (0*b*) (*e*); 1181 (2*b*) (*k*, *e*); 1308 (0) (*k*, *e*); 1417 (4*b*) (*k*, *i*, *e*); 1738 (8*vb*) (*e*); 2956 (6) (*k*, *e*); 3003 (3) (*k*).

4. *Monosodium malonate*, $Na^+ {}^-OOC\cdot CH_2\cdot COOH$. Aqueous solution containing 33 percent Eastman malonic acid, +1 equivalent c.p. NaOH. *p*H 4.2 to brom cresol green. $\Delta\nu$: 434 (5) (*k*, ±*e*); 586 (2*b*) (*e*); 664 (3*b*) (*k*, *e*); 802 (2*b*) (*k*, *e*); 923 (8*vb*) (*k*, *e*); 1193 (1*vb*) (*k*, *e*); 1278 ($\frac{1}{2}$) (*e*); 1372 (5) (*k*, *e*); 1408 (5*b*) (*k*, *e*); 1639 (0*vb*) (*e*) (water?); 1730 (2*b*) (*e*); 2943 (6) (*k*, *e*); 2987 (1) (*k*).

5. *Disodium malonate*, $Na^+\cdot {}^-OOC\cdot CH_2\cdot COO^-\cdot Na^+$. Aqueous solution containing 35 percent Eastman malonic acid, +2 equivalents NaOH. *p*H 7.2 (by brom thymol blue). $\Delta\nu$: 427 (3*b*) (*k*, *e*); 590 (3*b*) (*k*, *e*); 698 (1*b*) (*k*, *e*); 828 (3*b*) (*k*, *i*, *e*); 935 (6) (*k*, *i*, *e*); 956 (3) (*k*, *e*); 1181 (3) (*k*, *e*); 1260 (2*b*) (*k*, *e*); 1361 (6) (*k*, *e*); 1413 (6) (*k*, *e*); 1439 (6) (*k*, *e*); 1587 (1*vb*) (*k*, *e*); 2947 (6*b*) (*k*); 2984 (2*b*) (*k*).

6. *Malonic-d_2 acid-d_2*, DOOC·CD_2·COOD; 40 percent solution in D_2O. (For method of preparation see experimental section.) $\Delta\nu$: 412 (3) (*k*, *e*); 538 ($\frac{1}{2}$*b*) (*e*); 607 (1) (*k*, *e*); 733 (3) (*k*, *e*); 790 ($\frac{1}{2}$) (*k*, *e*); 845 (3) (*k*, *e*); 940±15 (0) (*k*, *e*); 1050 (4) (*k*, *e*); 1106 ($\frac{1}{2}$) (*k*); 1209 ($\frac{1}{2}$*b*) (*k*, *e*) (D_2O ?); 1360 (1) (*k*, *e*); 1719 (7*b*) (*e*); 2073 ($\frac{1}{2}$) (*k*); 2159 (5) (*k*, *e*); 2258 (3) (*k*, *e*).

7. *Disodium malonate-d_2*, $Na^+ {}^-OOC\cdot CD_2\cdot COO^{--} Na^+$; 35 percent solution in D_2O. (For method of preparation see experimental section.) $\Delta\nu$: 414 (1*b*) (*e*); 573±35 (1*vb*) (*e*) (double ?); 654 ($\frac{1}{2}$) (*e*); 810 (2) (*k*, *e*); 873 (3) (*k*, *e*); 910 (2) (*k*, *e*); 940 (1) (*k*, *e*); 1054 (4) (*k*, *e*); 1106 (1) (*k*, *e*); 1228 ($\frac{1}{2}$*vb*) (*k*, *e*) (D_2O ?); 1367 (4) (*k*, *e*); 1427 (7) (*k*, *i*, *e*); 1573 (2*b*) (*k*, *e*); 2076 (0) (*k*); 2153 (5) (*k*, *e*); 2238 (3) (*k*, *e*).

8. *Crotonic acid*, CH_3CH: CH·COOH. (Eastman, m.p. 70–72°) 8 percent solution in water, +0.2 *N* HCl. $\Delta\nu$: 415 (1*b*) (*e*); 513 (1*b*) (*k*, *e*); 690 (2*b*) (*k*, *e*); 850 (1*b*) (*k*, *e*); 916 (1*b*) (*k*, *e*); 994 (1*b*) (*k*, *e*); 1053 (1) (*k*, *e*); 1110 (1) (*k*, *e*); 1223 ($\frac{1}{2}$*b*) (*k*, *e*); 1302 (6) (*k*, *e*); 1383 (3) (*k*, *e*); 1451 (4) (*k*, *e*); 1658 (5) (*e*); 1700 (2) (*e*); 2939 (6) (*k*, *e*); 3061 (2) (*k*, *e*).

9. *Sodium crotonate*, CH_3CH : CH·$COO^- Na^+$; aqueous solution containing 22 percent Eastman crotonic acid, +0.96 equivalent NaOH. *p*H 6.2–6.3. $\Delta\nu$: 403 (3) (±*e*); 518 (1) (*k*, ±*e*); 730 (2*b*) (*k*, *e*); 865 (1) (*k*, *e*); 915 (1) (*k*, *e*); 1001 ($\frac{1}{2}$) (*k*, *e*); 1050 (1) (*k*, *e*); 1109 (1) (*k*, *e*); 1297 (5) (*k*, *e*); 1396 (4*vb*) (*k*, *e*); 1450 (4) (*k*, *e*); 1564 (0*vb*) (*e*?); 1661 (7*b*) (*e*); 2939 (4) (*k*, *e*); 3041 (2*b*) (*k*, *e*).

10. *Maleic acid* HOOC·CH : CHCOOH [*cis*]. 30 percent in water plus 0.5 *N* HCl. $\Delta\nu$ = 260 (2*b*) (*e*); 329 (1*b*) (*e*); 513 (1*vb*) (*k*, *e*); 624 (0*vb*) (double ?) (*k*, *e*); 750 (0) (*k*, *e*); 810 ($\frac{1}{2}$) (*k*, *e*); 869 (6) (*k*, *i*, *e*); 977 (2) (*k*, *e*); 1049 (1) (*k*, *e*); 1180 (5) (*k*, *e*); 1280 (0) (*k* ?); 1325 (1*b*) (*k*, *e*); 1390 (1*vb*) (*k*, *e*); 1654 (6*b*) (*e*); 1725 (6*vb*) (*e*); 2976 (4) (*k*, *e*).

11. *Disodium maleate* $Na^+ {}^-OOC\cdot CH$: $CHCOO^- Na^+$ [*cis*]. Aqueous solution, containing 36 percent maleic acid + two equivalents NaOH. $\Delta\nu$ = 258 (1*b*) (*e*); 339 (1*b*) (*e*); 482 (0) (*e*); 535 (0) (*e*); 903 (4) (*k*, *i*, *e*); 980 (2) (*k*, *e*); 1044 (0*b*) (*k*); 1193 (5) (*k*, *e*); 1306 (2) (*k*, *i*, *e*); 1400 (6) (*k*, *i*, *e*); 1434 (2) (*k*, *e*); 1570 (1*vb*) (*e* ?); 1647 (6) (*k*, *e*); 3038 (4) (*k*, *e*).

12. *Disodium fumarate* $Na^+ {}^-OOC\cdot CH$: CH·$COO^- Na^+$ [*trans*]. Solution containing 18 percent fumaric acid [Eastman, twice recryst.] + two equivalents of NaOH. $\Delta\nu$: 235 (1) (*e*); 307 (1) (*e*); 775 (0) (*k*, *e*); 905 (2) (*k*, *e*); 981 (2) (*k*, *e*); 1279 (5) (*k*, *i*, *e*); 1403 (6) (*k*, *i*, *e*); 1573 (1*b*) (*k*, *e*); 1657 (7*b*) (*e*); 3053 (4) (*k*).

13. *d-Tartaric acid*, HOOC·CHOH·CHOH·COOH (Eastman), m.p. 167–168°. 50 percent solution in water, +0.4 *N* HCl. $\Delta\nu$ = 367 (3) (*e*); 517 (3) (*k*, *e*); 601 (2) (*e*); 690 ($\frac{1}{2}$) (*k*, *e*); 754 (6) (*k*, *i*, *e*); 838 (1) (*k*, *e*); 894 (5) (*k*, *e*); 993 (3) (*k*, *e*); 1091 (2) (*k*, *e*); 1140 (2) (*k*, *e*); 1279 (4*vb*) (doublet ?) (*k*, *i*, *e*); 1413 (1) (*k*); 1442 (2) (*k*, *e*); 1630 (1*vb*) (*e*) (water ?); 1740 (5*b*) (*e*); 2950 (6*vb*) (*k*, *i*, *e*).

14. *Disodium d-tartrate*, $Na^+ {}^-OOC\cdot CHOH\cdot CHOH\cdot COO^- Na^+$; made from Eastman *d*-tartaric acid and 2 equivalents of c.p. NaOH. Solution contains 30 percent of tartaric acid, in water (Approx. 2 molar). $\Delta\nu$ = 239 ($\frac{1}{2}$*b*) (*e*); 378 (1*b*) (*e*); 491 (0) (*e*); 532 (2*b*) (*k*, *e*); 618 (1*b*) (*k*, *e*); 719 ($\frac{1}{2}$*b*) (*k*, *e*); 805 (4) (*k*, *e*); 844 ($\frac{1}{2}$) (*k*); 893 (4) (*k*, *e*); 992 (6) (*k*, *i*, *e*); 1068 (3*b*) (*k*, *e*); 1121 (3*b*) (*k*, *e*); 1224 (2*vb*) (*k*, *e*); 1310 (2*b*) (*k*, *e*); 1370 (5*b*) (*k*, *e*); 1418 (6*vb*) (*k*, *i*, *e*); 1617 (1*vb*) (*e*); 2936 (8*vb*) (*k*).

15. *Meso-tartaric acid*, HOOC·CHOH·CHOH·COOH (Eastman). 45 percent in water, +0.25 *N* HCl. $\Delta\nu$ = 233 (1*b*) (*e*); 376 (2*b*) (*e*); 532 (2*b*) (*k*, *f*, *e*); 669 (1*b*) (*k*, *e*); 739 (3*b*) (*k*, *e*); 817 (1) (*k*, *e*); 870 (3) (*k*, *i*, *e*); 937 (1) (*k*, *e*); 1009 (1) (*k*, *e*); 1119 (2*vb*) (*k*, *e*); 1252 (3*vb*) (*k*, *e*); 1432 ($\frac{1}{2}$*vb*) (*k*, *e*); 1632 (1*vb*) (*e*) (water ?); 1732 (5*vb*) (*e*); 2936 (6*vb*) (*k*, *e*).

16. *l-Aspartic acid hydrochloride*, HOOC·CH_2CH(NH_3^+·Cl^-)·COOH. (Aqueous solution, containing 30 percent by weight of Hoffman-LaRoche aspartic acid, + equivalent HCl, and excess HCl to 1.2 *N*.) $\Delta\nu$ = 393 (1*b*) (*e*); 533 (1*b*) (*k*, *e*); 624 ($\frac{1}{2}$) (*e*); 822 (4) (*k*, *f*, *e*); 898 ($\frac{1}{2}$) (*e*); 928 (3*b*) (*k*, *e*); 1007 (1) (*k*, *e*); 1087 ($\frac{1}{2}$) (*k*, *e*); 1151 ($\frac{1}{2}$) (*k*, *e*); 1258 (1*vb*) (*k*, *e*); 1367 ($\frac{1}{2}$) (*k*, *e*); 1418 (1) (*k*, *e*); 1634 ($\frac{1}{2}$) (*e*) (water); 1743 (4*vb*) (*e*); 2961 (4*vb*) (*k*, *i*, *e*) (double ?).

17. *Sodium l-aspartate*, $Na^+[{}^-OOC\cdot CH_2\cdot CH(NH_3^+)\cdot COO^-]$. Made from Hoffman-LaRoche aspartic acid and c.p. NaOH. Solution contained 26 percent of *l*-aspartic acid. *p*H 6.3±0.2 by indicators. $\Delta\nu$ = 533 ($\frac{1}{2}$) (*e*); 608 ($\frac{1}{2}$) (*e*); 732 (0) (*e*?); 858 (4) (*k*, *f*, *e*); 939 (4) (*k*, *e*); 983 ($\frac{1}{2}$) (*k*); 1085 (1*vb*) (*k*, *e*); 1140 (1*vb*) (*k*, *e*); 1227 (1*vb*) (*k*, *e*); 1330 (1) (*k*, *e*); 1355 (2) (*k*, *e*); 1411 (5*b*) (*k*, *i*, *e*); 1620±50 (1*vb*) (*e*) (water ?); 2935 (5*b*) (*k*, *e*); 2993 (2) (*k*).

18. *d-Glutamic acid hydrochloride*, HOOC·CH_2·CH_2·CH($NH_3^+Cl^-$)·COOH. (From Eastman *d*-glutamic acid, once recrystallized from hot water.) Solution containing 21 percent glutamic acid +HCl. Excess HCl to 0.5 *N*. $\Delta\nu$ = 345 (0) (*e*); 504 (0) (*k*, *e*); 639 (0) (*e*); 751 ($\frac{1}{2}$) (*k*, *e*); 804 ($\frac{1}{2}$) (*k*, *e*); 857 (2) (*k*, *e*); 917 (2) (*k*, *e*); 1098 ($\frac{1}{2}$) (*k*, *e*); 1347 ($\frac{1}{2}$) (*k*, *e*); 1433 (3) (*k*, *e*); 1649 ($\frac{1}{2}$*vb*) (*e*) (water ?); 1736 (4*vb*) (*e*); 2953 (6*b*) (*k*, *i*, *e*).

19. *Sodium d-glutamate*, $[{}^-OOC\cdot CH_2\cdot CH_2\cdot CH(NH_3^+)\cdot COO^-]Na^+$. Solution containing 32 percent Eastman *d*-glutamic acid (once recryst.) + one equivalent c.p. NaOH. *p*H 7.2±0.2 by brom thymol blue and phenol red. $\Delta\nu$: 655 (0*vb*) (*k*); 777 (0*b*) (*k*); 877 ($\frac{1}{2}$*b*) (*k*, *e*); 937 (4*b*) (*k*, *e*); 999 ($\frac{1}{2}$) (*k*, *e*); 1080 ($\frac{1}{2}$) (*k*, *e*); 1145 ($\frac{1}{2}$) (*k*, *e*); 1283 ($\frac{1}{2}$) (*k*); 1345 (2*b*) (*k*, *e*); 1410 (4*b*) (*k*, *i*, *e*); 1625±50 (2*vb*) (*e*) (water ?); 2943 (5*vb*) (*k*, *e*) (double ?).

20. *Tricarballylic acid*, $C_3H_5(COOH)_3$. (Eastman, m.p. 161–163°) 30 percent solution in water, +0.4 *N* HCl. $\Delta\nu$: 342 (0) (*e*); 424 (2*b*) (*e*); 540 ($\frac{1}{2}$) (*e*); 612 ($\frac{1}{2}$*b*) (*k*, *e*); 837 (3)

[21] J. H. Hibben, J. Chem. Phys. **3**, 675 (1935).

[22] H. Nisi, Jap. J. Phys. **7**, 1 (1931).

[23] For a complete list of references up to the end of 1935, see J. H. Hibben, Chem. Rev. **18**, 1 (1936). References and complete tables of Raman spectra up to about the same period are given by J. Weiler in Landolt-Börnstein's *Tabellen*, fifth edition, 3rd Ergänzungsband, Part II.

(k, f, e); 874 (2) (k, e); 930 (4) (k, i, e); 998 (0) (k); 1059 ($\frac{1}{2}$) (k, e); 1245 (1vb) (k, e); 1420 (5b) (k, i, e); 1724 (6b) (e); 2938 (6b) (k, i, e).

21. *Trisodium tricarballylate*, $Na_3^{+++}[C_3H_5(COO)_3]^{---}$. Solution containing 45 percent Eastman tricarballylic acid and three equivalents NaOH. pH 7.6±0.2 to phenol red. $\Delta\nu$: 327 ($\frac{1}{2}$) (e); 428 (2b) (e); 802 (1b) (k, e); 883 (4) (k, e); 948 (5b) (k, e); 1009 (2) (k, e); 1050 (1) (k, e); 1105 (1) (k, e); 1164 (1) (k, e); 1207 (1) (k, e); 1333 (3b) (k, e); 1419 (8b) (k, i, e); 1571 (1b) (k, e); 2934 (9vb) (k, i, e).

22. *Citric acid*, $C_3H_4(OH)(COOH)_3$, (Merck). 50 percent solution in water, with 0.4 N HCl. $\Delta\nu$: 253 (1b) (e); 396 (3b) (e); 525 (1b) (e); 605 (1b) (e); 723 (1) (k, e); 800 (5) (k, i, f, e); 903 (1) (k, e); 939 (6) (k, e); 1056 (3) (k, e); 1130 (1b) (k, e); 1200 (1) (k, e); 1403 (3) (k, e); 1438 (2) (k, e); 1731 (6b) (e); 2948 (6) (k, i, e); 3001 (1) (k).

23. *Trisodium citrate*, $Na_3^{+++}[C_3H_4(OH)(COO)_3]^{---}$. Solution containing 30 percent Merck's citric acid in water, with 3 equivalents NaOH. pH 7.4−7.6 by phenol red. $\Delta\nu$: 233 ($\frac{1}{2}$) (e); 317 (0) (e); 409 (1b) (e); 583 ($\frac{1}{2}vb$) (e); 845 (4) (k, e); 956 (5) (k, i, f, e); 1045 (1b) (e); 1100 (1b) (k, e); 1210 ($\frac{1}{2}$) (e); 1302 (0) (e); 1415 (8b) (k, i, e); 1580 ($\frac{1}{2}b$) (e); 2929 (5) (k, e); 2982 (1) (k).

Polarization Studies: Examination by the technique previously described[3] showed the following lines to be strongly polarized ($\rho \ll 6/7$) malonic acid: 590, 773, 919, 1738. Disodium malonate: 590, 828, 935, 1361(?), 1439. Dipotassium oxalate: 902, 1457, 1489.

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The Rotation and Vibration of Linear Triatomic Molecules

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The rotation and vibration of a linear molecule cannot be treated by the method of rotating axes if it contains more than three atoms. The definition of the axes for the triatomic case may be based on the fact that the three atoms always determine a plane. The relation of this definition to that for the nonlinear molecules is discussed, and the appropriate normal coordinates are introduced. The wave equation of the problem is derived and its approximate solution is discussed. The fact that the Eulerian angles do not enter into the zero- and first-order terms of the Hamiltonian makes it possible to calculate some of the second order terms of the expression for the energy values with complete generality. These are the terms that arise from the rotation and from the coupling between the rotation and vibration. They are found to be

$$\hbar^2[J(J+1)-l^2]/2A+C,$$

where A is the value of the moment of inertia at equilibrium, and

$$C=[\hbar^2(V_2+1)/2A]\{s^2(V_1+\tfrac{1}{2})[(\omega_1/\omega_2)+(\omega_2/\omega_1)] +c^2(V_3+\tfrac{1}{2})[(\omega_3/\omega_2)+(\omega_2/\omega_3)]\}-\hbar^2/2A.$$

In this expression, the V's are the vibrational quantum numbers and the ω's are the natural frequencies. The index 2 refers to the perpendicular vibration. The quantities c and s are determined by the potential energy function and are related by $c^2+s^2=1$. For symmetric molecules, $X-Y-X$, their values are $c=1$, $s=0$. If the natural frequencies are commensurable, the derivation ceases to be valid, but it appears likely that the result is essentially the same in this case.

INTRODUCTION

THE general theory of the interaction of the rotation and vibration of normal polyatomic molecules has been discussed by Eckart[1] and by Wilson and Howard.[2] They found it convenient to exclude linear molecules by their definition of normality. In an investigation preliminary to this one, it was found that the method developed by these authors cannot be extended, in general, to apply to linear molecules. More general schemes are needed, such as those considered by Welker.[3] These methods are also applicable to other anomalous molecules, such as ethane.

However, the method of rotating axes can still be used for the particular case of a triatomic linear molecule. The definition of the axes is then essentially that used by Dennison.[4] In the first part of this paper, it will be shown how this this definition is related to that given in references 1 and 2 for the nonlinear molecules. The Hamiltonian will be derived in the second part and in the third, the solution of the wave equation and calculation of the energy values will be discussed. In the concluding part, this calcu-

* The first and second parts of this paper are based on a master's thesis entitled "The Quantum Mechanical Hamiltonian for Triatomic Linear Symmetric Molecules" submitted to the University of Chicago by A. W.

[1] C. Eckart, Phys. Rev. **47**, 552 (1935).

[2] E. B. Wilson, Jr., and J. B. Howard, J. Chem. Phys. **4**, 260 (1936).

[3] H. Welker, Zeits. f. Physik **101**, 95 (1936).

[4] D. M. Dennison, Rev. Mod. Phys. **3**, 292 (1931).

lation will be compared with that made by Adel and Dennison[5] for the CO_2 molecule.

The Moving Axes

In order to define a set of rotating axes, the position of its origin and the directions of its axes must be specified; six independent equations are needed to accomplish this. In the general case of a nonlinear molecule, the requirement that the origin be at the centroid of the molecule furnishes three equations, and the remaining three are obtained from Casimir's condition.[6, 1, 2] This condition requires that the angular momentum of the molecule relative to the moving axes shall vanish as the equilibrium configuration is approached, regardless of the direction (in phase space) from which that approach is made. For a linear molecule, the three equations thus obtained are not independent. Additional independent and simple equations cannot be found in general, but for the triatomic molecule they are furnished by Dennison's requirement that the plane of the three atoms always coincide with one of the coordinate planes of the moving axes.

Using the notation of reference 1, let the rectangular coordinates of the ath atom relative to the moving system be y_{xa}, y_{ya}, y_{za}; in the present case, $a=1, 2, 3$. Let the equilibrium values of these coordinates be z_{ia}, and the normal coordinates be q_λ ($\lambda=1, 2, 3$). Then

$$y_{ia}=z_{ia}+\Sigma_\lambda q_\lambda z_{\lambda,ia} \tag{1}$$

with $z_{\lambda,ia}$ independent of the q_λ. The equations defining the axes are to be expressed in terms of the y_{ia} and are not to involve the q_λ explicitly. However, they must be satisfied identically when the y_{ia} are eliminated by means of Eq. (1).

The requirement that the plane of the molecule is also the yz plane of the axes is

$$y_{xa}=0, \quad a=1, 2, 3. \tag{2}$$

The equations fixing the origin at the centroid are (m_a mass of the ath atom)

$$\Sigma_a m_a y_{ia}=0, \tag{3}$$

of which only two are independent of Eq. (2). The angular momentum relative to the moving axes will always be a vector parallel to the x axis (because of Eq. (2)) and hence Casimir's condition furnishes just one additional equation, bringing the total to six as required. This equation is

$$\lim_{y_{ia}\to z_{ia}} \{\Sigma_a m_a(y_{ya}\dot{y}_{za}-y_{za}\dot{y}_{ya})\}=0. \tag{4}$$

The requirement that these equations be satisfied for all values of the q_λ and $\dot{q}_\lambda$ imposes certain restrictions on the constants z, but not enough to determine them uniquely. In other words, these equations define a class of moving coordinate systems, such that each is stationary relative to all others of the class. It is still possible to choose one member of the class at will. The requirement that the q_λ be normal coordinates also limits the values of the z's, but the choice may still be made so that at equilibrium, the z axis passes through each of the three atoms. It is usually supposed that the normal vibrations of a linear molecule are either of the $\parallel$ or of the $\perp$ type.[4] With this assumption, the selection just made reduces the Eq. (1) to the form

$$y_{ya}=Y_a q_2, \quad y_{za}=z_a+Z_a' q_1+Z_a'' q_2, \tag{1.1}$$

where Y, Z', Z'' are constants replacing the $z_{\lambda,ia}$. The requirement that Eq. (3) be identically satisfied leads to

$$\Sigma_a m_a z_a=\Sigma_a m_a Y_a= \Sigma_a m_a Z_a'=\Sigma_a m_a Z_a''=0 \tag{3.1}$$

and Eq. (4) to

$$\Sigma_a m_a Y_a z_a=0. \tag{4.1}$$

These equations determine Y_a as a function of z_a except for an arbitrary normalizing factor:

$$Y_1=(z_2-z_3)[m_2 m_3/m_1(m_1+m_2+m_3)]^{\frac{1}{2}}, \text{ etc.} \tag{5.1}$$

The normalizing factor has been so chosen that

$$\Sigma_a m_a Y_a^2=\Sigma_a m_a z_a^2=A; \tag{6}$$

A is thus the equilibrium value of the moment of inertia of the molecule. This choice makes the q_λ dimensionless; in quantum-mechanical prob-

[5] A. Adel and D. M. Dennison, Phys. Rev. **43**, 716 (1933); **44**, 99 (1933).

[6] H. B. G. Casimir, *The Rotation of a Rigid Body in Quantum Mechanics*, Chap. V. Dissertation, Leyden (1931).

lems they may be treated as small quantities of the order of magnitude $\epsilon=(\hbar/A\omega)^{\frac{1}{2}}$, ω being one of the natural frequencies. The constants Z_a' and Z_a'' are not completely determined, but the requirement that the q_λ be normal coordinates imposes the further conditions

$$\begin{aligned}\Sigma_a m_a Z_a'^2=\Sigma_a m_a Z_a''^2=A,\\ \Sigma_a m_a Z_a' Z_a''=0.\end{aligned} \tag{7}$$

The Eqs. (3.1) and (7) are equivalent to

$$\begin{aligned}Z_a'&=cz_a-sY_a,\\ Z_a''&=sz_a+cY_a,\\ c^2+s^2&=1,\end{aligned} \tag{8}$$

so that only one constant is undetermined after the equilibrium configuration is given.

The Hamiltonian Operator

The determination of the classical Hamiltonian kinetic energy is now a straightforward algebraic calculation if the results of reference 1 are utilized. The first step is the calculation of the components of the moment of inertia tensor in the moving system. These are

$$\begin{aligned}A_{xx}&=A_{yy}+A_{zz},\\ A_{yy}&=A(f^2+g^2),\\ A_{zz}&=Aq_2^2,\\ A_{yz}&=-Aq_2f,\\ A_{xy}&=A_{xz}=0,\end{aligned} \tag{9}$$

where $f=-sq_1+cq_3$, $g=1+cq_1+sq_3$.

The second step is the calculation of the angular momentum relative to the moving axes: the result is

$$\begin{aligned}\Lambda_x&=\Sigma_a m_a(y_{ya}\dot{y}_{za}-y_{za}\dot{y}_{ya})\\ &=A\{s(q_1\dot{q}_2-q_2\dot{q}_1)+c(q_2\dot{q}_3-q_3\dot{q}_2)\},\\ \Lambda_y&=\Lambda_z=0.\end{aligned} \tag{10}$$

The components of the total angular momentum of the molecule along the moving axes are (cf. Eq. (8), reference 1)

$$\begin{aligned}M_x&=A_{xx}\Omega_x+\Lambda_x,\\ M_y&=A_{yy}\Omega_y+A_{yz}\Omega_z,\\ M_z&=A_{yz}\Omega_y+A_{zz}\Omega_z,\end{aligned} \tag{11}$$

the Ω_i being the components of the angular velocity, again along the moving axes. The momenta conjugate to the q_λ are (cf. Eq. (11), reference 1)

$$p_\lambda=A\dot{q}_\lambda+\Omega_x(\partial\Lambda_x/\partial\dot{q}_\lambda). \tag{12}$$

The Eq. (11) and (12) are now to be solved for the Ω_i and $\dot{q}_\lambda$:

$$\begin{aligned}\Omega_x&=[M_x-c\Lambda_1-s\Lambda_3]/Ag^2,\\ \Omega_y&=[M_y+fM_xq_2^{-1}]/Ag^2,\\ \Omega_z&=M_z/Aq_2^2+f\Omega_y/q_2;\\ \dot{q}_1&=p_1/A+sq_2\Omega_x,\\ \dot{q}_2&=p_2/A+f\Omega_x,\\ \dot{q}_3&=p_3/A-cq_2\Omega_x.\end{aligned} \tag{13}$$

The following abbreviations have been used in Eq. (13):

$$\Lambda_1=q_2p_3-p_2q_3,\quad \Lambda_3=q_1p_2-p_1q_2. \tag{14}$$

The kinetic energy is then obtained by adding the products of the momenta with their corresponding velocities:

$$\begin{aligned}2AT=p_1^2+p_2^2+p_3^2+M_x^2/q_2^2\\ +[M_x-c\Lambda_1-s\Lambda_3]^2/g^2\\ +[M_y+fM_xq_2^{-1}]^2/g^2.\end{aligned} \tag{15}$$

It will be noted that the moments of inertia A_{xx} and A_{yy} do not appear in this equation.

The kinetic energy operator cannot be obtained from Eq. (15) by merely replacing the momenta by appropriate operators; if this were done, the result would not be a real operator. The appropriate additional factors are easily determined by the method of Wilson and Howard.[2] The resulting operator may be divided into two parts:

$$\begin{aligned}2AT_0=g^{-2}p_1g^2p_1+g^{-2}p_3g^2p_3\\ +q_2^{-1}p_2q_2p_2+M_x^2q_2^{-2},\end{aligned} \tag{16}$$

and

$$\begin{aligned}2AT_2=g^{-2}q_2^{-1}[M_x-c\Lambda_1-s\Lambda_3]q_2[M_x-c\Lambda_1-s\Lambda_3]\\ +g^{-2}[M_y+fM_xq_2^{-1}]^2.\end{aligned} \tag{17}$$

It is readily seen that the contribution of T_0 to the energy value is of the order of magnitude

$\hbar\omega$, while that of T_2 is of order $\epsilon^2\hbar\omega=\hbar^2/A$. There are no terms that make contributions of order $\epsilon\hbar\omega$, which is a direct consequence of Casimir's condition.

The potential energy, U, will depend only on the q_λ and will contain terms of every order of magnitude. The zero-order terms will be

$$U_0=(A/2)(\omega_1^2q_1^2+\omega_2^2q_2^2+\omega_3^2q_3^2); \quad (18)$$

the appearance of the moment of inertia, A, in this expression is a purely formal consequence of the normalization of Eq. (6). The complete Hamiltonian operator is thus

$$H=(T_0+U_0)+U_1+(T_2+U_2)+\cdots, \quad (19)$$

the terms being bracketed according to order of magnitude.

In order to determine the characteristic values of this operator, it is necessary to consider the domain of the coordinates q_λ, and the conditions to be imposed on the wave function at the boundaries of that domain. Because of the small numerical value of ϵ in practical problems the wave function will have appreciable values only in a very small region in the interior of the domain, and it is easily seen that the characteristic values will not depend strongly on the boundary conditions. It is therefore desirable to transform the Hamiltonian in such a manner that the domain may be treated as infinite in all directions, and that the usual boundary conditions for such domains may be imposed. This end may be attained in three stages. The first is the contact transformation

$$H'=gHg^{-1}. \quad (20)$$

As is well known,[7] the characteristic values of H and H' are identical, provided that the boundary conditions for H' are suitably derived from those for H. This transformation eliminates g from T_0, but not from T_2. The second step is the replacement of g in T_2 by its Taylor expansion. The justification of this expansion is not obvious, but in view of the previous expansion of the potential energy, it is useless to consider its justification at this point. The final replacement of the correct domain and boundary conditions by the simpler ones will produce changes in the characteristic values, but these will presumably be negligible.

The kinetic energy operators as thus simplified are

$$2AT_0'=p_1^2+p_3^2+q_2^{-1}p_2q_2p_2+q_2^{-2}M_z^2, \quad (21)$$

$$2AT_2'=g^{-1}q_2^{-1}[M_x-c\Lambda_1-s\Lambda_3]q_2[M_x-c\Lambda_1-s\Lambda_3]g^{-1}+g^{-2}[M_y+fM_zq_2^{-1}]^2. \quad (22)$$

For many purposes, it is permissible to neglect terms of order $\epsilon^3\hbar\omega$ or smaller. Then g may be replaced by unity. This will be done for the remainder of this paper.

The Perturbation Calculation

This Hamiltonian has certain characteristics that simplify some parts of the second order perturbation calculation. For convenience, let u always denote a function independent of the Eulerian angles α, β, γ, and v always denote a function of α, β only, independent of the other variables. Then, since the zero-order Hamiltonian depends only on M_z^2, on the q_λ, and on their momenta, the zero-order wave function will have the form

$$\psi_0=vu(N,l)\exp(\pm il\gamma), \quad (23)$$

where v and the sign of the exponent are undetermined. The determination of $u(N, l)$ and of the zero-order energy, W_0, has been discussed in detail by Dennison;[4] they are

$$W_0(N)=(V_1+\tfrac{1}{2})\hbar\omega_1+(V_2+1)\hbar\omega_2+(V_3+\tfrac{1}{2})\hbar\omega_3,$$
$$u(N,l)=\psi^{V_1}(q_1)\psi^{V_3}(q_3)R^{V_2,\,l}(q_2), \quad (24)$$

where ψ^V and $R^{V,\,l}$ are one- and two-dimensional Hermite functions, respectively. The three quantum numbers V_λ have been abbreviated as N; all the quantum numbers have integral values, and

$$l=V_2,\ V_2-2,\ V_2-4,\cdots \quad 1 \text{ or } 0. \quad (25)$$

For the present, it will be supposed that ω_1, ω_2 and ω_3 are incommensurable numbers, so that accidental degeneracy may be avoided. Since the first-order terms of the Hamiltonian depend only on the q_λ, the function v will re-

[7] Dirac, *Quantum Mechanics* (Oxford, 1935), p. 109; Condon and Morse, *Quantum Mechanics* (McGraw-Hill), pp. 59, 71.

main undetermined by the first-order calculation. The first-order wave function will be

$$\psi=[v_+ \exp(il\gamma)+v_- \exp(-il\gamma)] \times[u(N,l)+\sum_{n\neq N} u(n,l)a(n)], \quad (26)$$

the constants $a(n)$ being given by the usual formula.

The second-order terms of the Hamiltonian involve all coordinates or their momenta; since some of these have not appeared in earlier terms, the usual linear secular equations will be replaced by differential equations determining the functions v_+ and v_-. These equations can be written most conveniently by first defining the four linear operators T_{++}, T_{+-}, etc.:

$$T_{\pm\pm}v=\int\int |u(N,l)^* \exp(\mp il\gamma) \times[T_2'u(N,l)v \exp(\pm il\gamma)]\}q_2dqd\alpha. \quad (27)$$

The secular differential equations are then

$$\begin{aligned} T_{++}v_+ + T_{+-}v_- &= W''v_+, \\ T_{-+}v_+ + T_{--}v_- &= W''v_-, \end{aligned} \quad (28)$$

and the second-order energy correction is

$$W_2 = W'' + \text{ terms arising from } U_1 \text{ and } U_2.$$

On substituting the expression for T_2' from Eq. (22) into Eq. (27), it is found that many terms vanish because of the properties of the M operators, and without reference to the special form of $u(N, l)$. The result of the calculation is that

$$\begin{aligned} T_{+-}=T_{-+}&=0, \\ T_{++}=T_{--}&=[(M_x^2+M_y^2)/2A]+C, \end{aligned} \quad (29)$$

where

$$C=\frac{\hbar^2l^2}{2A}\int q_2^{-1}|(-sq_1+cq_3)u(N,l)|^2dq + (1/2A)\int q_2|(c\Lambda_1+s\Lambda_3)u(N,l)|^2dq. \quad (30)$$

From Eq. (29) it follows that the $\pm$ degeneracy is not removed by the second-order perturbation. Since the characteristic values of $M_x^2+M_y^2$ are $\hbar^2[J(J+1)-l^2]$ with $J=l, l+1, \cdots$, the values of W'' can be written down at once. The functions $v_\pm$ are also immediately available: they are essentially the wave functions of the symmetric rotator.[4]

Using the explicit form of $u(N, l)$ (Eq. (24)) the quantity C can be evaluated. For this calculation it is convenient to use the relation

$$\int q_2\{(\partial R/\partial q_2)^2+R^2l^2/q_2^2\}dq_2=A\omega_2(V_2+1)/\hbar,$$

which follows at once from the differential equation for R. The result is that

$$C=[\hbar^2(V_2+1)/2A]\{s^2(V_1+\tfrac{1}{2})[(\omega_1/\omega_2)+(\omega_2/\omega_1)] +c^2(V_3+\tfrac{1}{2})[(\omega_3/\omega_2)+(\omega_2/\omega_3)]\}-\hbar^2/2A. \quad (31)$$

The appearance of the ratios of the natural frequencies in this expression is in accord with expectation.[1] This part of the energy expression is determined by the lack of rigidity of the molecule, and in quantum theory, a small natural frequency implies a large amplitude of oscillation. This part of the energy expression should therefore become large when any one of the natural frequencies becomes small. Thus each frequency should appear as a denominator. Since dimensional arguments show that the frequencies can enter into the second-order energy only as ratios, the general form of Eq. (31) may be expected to be valid in more general cases than the one here treated.

The Carbon Dioxide Molecule

The most interesting linear triatomic molecule is that of carbon dioxide. It has two special characteristics: it is symmetric, the structure being O−C−O, and the frequency ω_1 is very nearly equal to $2\omega_2$. The first results in fixing the values of c and s at 1 and 0, respectively. The second results in accidental degeneracy, which was excluded in the previous section. However all conclusions there derived, except Eq. (31), remain valid if the functions $u(N, l)$ are replaced by the appropriate linear combinations obtained from the solution of the first-order secular equations. These combinations have been calculated by Adel and Dennison.[5]

A comparison of their Hamiltonian with the

present one reveals only one important difference, though there are numerous minor ones. Using $c=1$, $s=0$, it is seen that Λ_3 will disappear from the Hamiltonian, but $\Lambda_1=q_2p_3-p_2q_3$ will remain. In the Hamiltonian of Dennison and Adel, only the term q_2p_3 appears.[8] Had there been no accidental degeneracy, this would have resulted in the omission of the term ω_2/ω_3 in Eq. (31), and the retention of the term ω_3/ω_2. Apparently, it will have a similar effect when there is accidental degeneracy. Fortunately, $\omega_3/\omega_2=3.55$, so that the relative numerical error is small. From an examination of the published calculations, it is not possible to conclude with certainty that this is the only effect of the omission. If there are no others, one may also conclude that Eq. (31) remains valid even when the accidental degeneracy is taken into account.

[8] In their notation, $q_2^2p_3^2=(\omega_2/2\omega_3 I)\rho^2p_\xi^2$.

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The Diffusion Constant of an Electrolyte, and Its Relation to Concentration

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A semi-empirical equation is proposed which predicts for potassium chloride, sodium chloride and potassium nitrate in aqueous solution, differential diffusion constants which agree with the experimentally determined values for the three salts within the limits of error of the experiments. The relation of the effective diffusion constant determined in the Northrop-McBain diaphragm cell to the differential diffusion constant is discussed; it is shown that Cole and Gordon's rule that the effective diffusion constant measured in such a cell is equal to the differential diffusion constant for the mean concentration, is still a valid approximation even when there is a nonlinear dependence of diffusion constant on cencentration, provided the total concentration range involved is less than 0.1 *N*.

IT has long been recognized that there is a relation between the thermodynamic properties of solutions of a given solute and the diffusion constant k of that solute; the Nernst equation connecting the osmotic pressures and mobilities of the ions of an electrolyte with diffusion constant at infinite dilution is a familiar example. It has also been recognized that the diffusion constant k, defined by the Fick equation (for unidirectional diffusion in the x direction)

$$\frac{\partial c}{\partial t}=\frac{\partial}{\partial x}\left(k\frac{\partial c}{\partial x}\right), \tag{1}$$

where c is the concentration and t the time, is in general itself a function of concentration. As a result, it is necessary to distinguish between the true "differential" diffusion constant at a given concentration, and "integral" diffusion constants which represent some sort of average depending on the kind of apparatus used. Since in most cases it is the integral diffusion constant that is measured, and since it is necessary to know the relation between the differential diffusion constant and concentration to interpret the integral values, it is evident that this relation is a matter of some importance.

Onsager and Fuoss[1] in an important paper seem to have made the first attempt to compute the dependence of k on c. Their method consisted essentially in equating the diffusion constant to the product of two terms; the first of these involved the change in thermodynamic potential of the solute with concentration, and the second was a "mobility" term which for infinite dilution reduced to the familiar Nernst expression. The thermodynamic term was evaluated from the empirically determined activity coefficients of the electrolyte, and the mobility term was calculated by means of the Debye-Onsager theory of conductivity. Their evaluation of this latter item was admittedly unsatisfactory, and the agreement with experiment in the two cases they studied (sodium and potassium

[1] Onsager and Fuoss, J. Phys. Chem. **36**, 2689 (1932).

TABLE I. *KCl at 25°C; $k_0 = 1.993 \times 10^{-5}$ cm²/sec.*

m	$1+m\partial \ln \gamma/\partial m$	$V/n_1\bar{V}_1$	η_0/η	$10^5 \cdot k$
0.01	0.9532	1.0002	1.000	1.900
.02	.9392	1.0005	1.000	1.873
.05	.9180	1.0013	1.000	1.832
.10	.9025	1.0027	1.001	1.805
.20	.8909	1.0056	1.002	1.789
0.50	.8902	1.0144	1.003	1.805
1.00	.9085	1.0299	1.005	1.874
1.50	.9295	1.0460	1.003	1.944
2.00	0.9500	1.0625	0.998	2.008

TABLE II. *$10^5 \cdot k$ at 18.5°.*

m	KCl	NaCl	KNO_3
0	1.694	1.354	1.645
0.05	1.559	1.246	1.483
.10	1.535	1.227	1.428
.20	1.522	1.214	1.37
0.50	1.540	1.219	1.29
1.00	1.604	1.243	
1.50	1.666	1.263	
2.00	1.723	1.273	

chlorides) was only semi-quantitative, the discrepancies for 1 N being 12.5 percent and 3.4 percent, respectively; their calculation did, however, predict the correct shape for the curves of k against $\sqrt{c}$. It is the present purpose to show that a simpler empirical relation[2] gives the diffusion constant in the few cases where the data are available within the limits of error of the experiments; the discussion is limited to the 1–1 type of electrolyte since it is only for these that the necessary information is now available, but the extension to other types is obvious.

If k be the differential diffusion constant at concentration c moles per cc, and if k_0 be the value of k for $c=0$, it is assumed that

$$k = (k_0/2RT) \cdot (c\partial\mu_2/\partial c) \cdot (\eta_0/\eta). \qquad (2)$$

Here μ_2 is the potential of the solute in a solution containing in V cc n_1 moles water and n_2 moles solute; η_0 and η are the macroscopic viscosities of water and solution; and k_0 is given by the Nernst relation

$$k_0 = (2RT/F^2) \cdot (u_1u_2/(u_1+u_2)) \qquad (3)$$

where F is Faraday's constant and u_1 and u_2 are the mobilities at infinite dilution of anion and cation, respectively. It is evident from inspection that Eq. (2) reduces to an identity for $c=0$, since $c\partial\mu_2/\partial c$ approaches $2RT$. Eq. (2) may be written in the more useful form

$$k = (k_0/2RT) \cdot (n_2\partial\mu_2/\partial n_2) \cdot (V/n_1\bar{V}_1) \cdot (\eta_0/\eta) \qquad (4a)$$

$$= k_0(1+m\partial \ln \gamma/\partial m) \cdot (V/n_1\bar{V}_1) \cdot (\eta_0/\eta) \qquad (4b)$$

since $c = n_2/V$, and $\mu_2 = \phi(T, P) + 2RT \ln \gamma m$, where m is the molality (equal to $55.51n_2/n_1$) and γ is the activity coefficient; $\bar{V}_1$ is the partial molal volume of the water in the solution. Alternatively, (4a) may be written

$$k = -(k_0/2) \cdot (n_1\partial \ln a_1/\partial n_2) \cdot (V/n_1\bar{V}_1) \cdot (\eta_0/\eta), \qquad (4c)$$

where a_1 is the activity of the water. Eqs. (4b) and (4c) are in a form suitable for calculation when information as to activity coefficients or vapor pressures is available.

To illustrate the magnitude of the various factors in Eq. (4), the calculation for potassium chloride at 25°C is summarized in Table I; the value for k_0 was computed from the data of MacInnes, Shedlovsky and Longsworth,[3] the activity coefficients are those of Harned,[4] and the viscosity and density data from *International Critical Tables*.[5] Table II gives the results of similar calculations[6] for KCl, NaCl and KNO_3 at 18.5°, and the results of Tables I and II are shown graphically in Fig. 1, the abscissa here being the square root of the normality.

The only unambiguous determinations of differential diffusion constants are those of

[2] The relation (in this notation)

$$k = (k_0/2RT) \cdot (c\partial\mu_2/\partial c)$$

was proposed by E. Schreiner in Tidsskrift for Kemi Bergvaesen **2**, 151 (1922); cf. Chem. Abstracts **17**, 3126. I have to thank the referee for calling this to my attention.

[3] MacInnes, Shedlovsky and Longsworth, J. Am. Chem. Soc. **54**, 2758 (1932).

[4] Harned, J. Am. Chem. Soc. **51**, 416 (1929).

[5] *International Critical Tables* III, p. 87 and V, p. 17.

[6] For KCl, activity coefficients for 18.5° were computed from Harned's valūes for 25° by means of the calorimetrically determined heats of solution (Wüst and Lange, Zeits. f. physik. Chemie **116**, 161 (1925); Lange and Monheim, Zeits. f. physik. Chemie **A150**, 349 (1930)). For NaCl, the activity coefficients are those of Harned and Nims (J. Am. Chem. Soc. **54**, 423 (1932)). For KNO_3, the activity coefficients up to 0.1 molal are those of Scatchard, Prentiss and Jones (J. Am. Chem. Soc. **54**, 2690 (1932)) corrected from the freezing point to 18.5° by means of Lange and Monheim's data; for higher concentrations, the isopiestic vapor pressure measurements of Robinson were employed (J. Am. Chem. Soc. **57**, 1165 (1935)); since these are for 25°, the calculation was not carried beyond 0.5 molal because of the lack of reliable heat of dilution data for this salt at concentrations greater than 0.1 m. All density and viscosity data are from *International Critical Tables*.

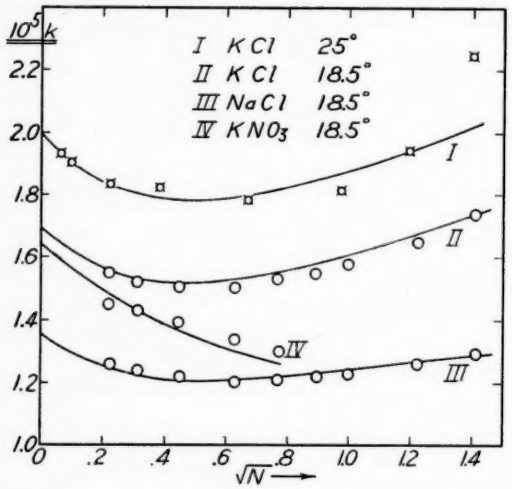

FIG. 1.

Clack,[7] who worked with potassium chloride, sodium chloride and potassium nitrate at 18.5°C. His method consisted in determining the gradient of refractive index and consequently of concentration in a diffusing column of liquid at the steady state; from this and the total amount of solute diffused through the column in a known time, he was able to compute k. His results for the three salts are indicated by the circles in Fig. 1, and it is at once evident that the calculated curves agree in general with the experimental points within his apparent experimental error ($\pm 0.02\times 10^{-5}$). Clack's measurements provide a particularly good test of Eq. (2), since the factor η_0/η is actually greater than unity for KCl and KNO_3 over almost the entire range of concentration, while it is markedly less than unity for NaCl (0.922 at 1 m, 0.839 at 2 m); moreover, owing to the abnormally small activity coefficient of potassium nitrate, the factor $n_2\partial\mu_2/\partial n_2$ is only 0.746 for this salt at 0.5 m, compared with 0.927 for sodium chloride and 0.887 for potassium chloride at the same concentration.

McBain and Dawson[8] have recently investigated the effect of concentration on the diffusion constant of potassium chloride at 25° using the two-compartment diaphragm cell originally employed by Northrop and Anson;[9] this apparatus is of such general utility in diffusion measurements that it is well worth while to consider the nature of the results that are obtained from it. In effect, the method consists in allowing a solution of known concentration to diffuse down through a sintered glass diaphragm for a known time into an equal volume of pure solvent; the pore size of the diaphragm is such that diffusion takes place unhindered but that streaming of the solution as a whole cannot occur. Since the densest solution in each compartment tends to be at the top, the contents of each compartment are stirred automatically as the diffusion proceeds, and so are of uniform composition throughout. On the assumption that Fick's law is obeyed, Barnes[10] has shown that to a high order of approximation the concentrations of the upper and lower solutions (c' and c'') at a time ϑ are given by

$$c' = (c_0/2)\cdot(1+\exp[-\beta k\vartheta]), \qquad (5a)$$

$$c'' = (c_0/2)\cdot(1-\exp[-\beta k\vartheta]), \qquad (5b)$$

where c_0 is the initial concentration of the upper solution, k is the diffusion constant (assumed independent of concentration) and β is a cell factor which depends only on the geometry of the apparatus and which can be determined once and for all by calibrating the cell with a solute of known k.

In the usual cell, the concentrations of the upper and lower solutions are changing so slowly that the condition obtaining in the diaphragm is practically that for a steady state; if this be the case, Cole and Gordon[11] have shown that the apparent diffusion constant k', computed from the observed amount of solute diffusing per second from concentration c' to concentration c'', is related to the differential diffusion constants by the equation

$$k'(c'-c'') = \int_{c''}^{c'} k\cdot dc. \qquad (6)$$

If k be a linear function of c, k' by Eq. (6) must be equal to k for a concentration $(c'+c'')/2$, and since in a Northrop-McBain cell $(c'+c'')/2$ is constant throughout an experiment, it follows that an effective diffusion constant, computed from observed values of c', c'' and ϑ by means of

[7] Clack, Proc. Phys. Soc. **36**, 313 (1924).
[8] McBain and Dawson, Proc. Roy. Soc. **A148**, 32 (1935).
[9] Northrop and Anson, J. Gen. Physiol. **12**, 543 (1929).
[10] Barnes, Physics **5**, 4 (1934).
[11] Cole and Gordon, J. Phys. Chem. **40**, 733 (1936).

Eq. (5), will in this case be equal to the differential diffusion constant for a concentration $(c'+c'')/2$.

Cole and Gordon's rule, however, is not necessarily valid when, as in dilute solutions of the electrolytes, k is far from a linear function of concentration. It can easily be shown, however, that if k' be the apparent diffusion constant given by Eq. (6) for concentrations c' and c'' existing at the time t, then the effective diffusion constant $\bar{k}$ (computed as before from observed c', c'' and ϑ by means of Eq. (5)) will be related to the k' involved, by the relation[12]

$$\int_0^{\vartheta} k' \cdot dt = \bar{k}\vartheta. \qquad (7)$$

The relation of $\bar{k}$ to the differential diffusion constant can perhaps be best illustrated by a numerical example. Consider an experiment where 0.1 N KCl at 25°C is allowed to diffuse into water. (With such dilute solutions, normality and molality may be taken as identical.) Assume that the apparatus and time of diffusion are such that at the end of the experiment the upper concentration has fallen to 0.0684 N and the lower has risen to 0.0316 N, i.e., $\beta\bar{k}\vartheta = 1.0$, a typical value in such experiments. To a close enough approximation the c' and c'' throughout the experiment for various values of t/ϑ may be computed by means of Eq. (5) (see Table III, columns 2 and 3), and from these, by means of Eq. (6) and Table I, the k' listed in the fourth column may be obtained; from these again by means of Eq. (7), $\bar{k} = 1.836 \times 10^{-5}$. It is important to note that had the diffusion been stopped when the upper and lower concentrations were 0.075 N and 0.025 N, respectively, $\bar{k}$ would have been 1.839×10^{-5}, a value differing only by one-sixth of a percent from that resulting from the longer diffusion. It is doubtless due to this circumstance that effective diffusion constants calculated from experiments lasting for varying times with this type of apparatus are in such close agreement. It is also important to note that $\bar{k}$ is very close to k for 0.05 N *viz.* 1.832×10^{-5}; calculations similar to those of Table III for the diffusion of 0.02 N and 0.01 N KCl into water (with $\beta\bar{k}\vartheta = 1.0$ as before) predict $\bar{k}$ of 1.905 and 1.928×10^{-5}, respectively, which once again are very near to the values of k for 0.01 N and 0.005 N, 1.900 and 1.926×10^{-5}. Thus in the Northrop-McBain cell, even with a nonlinear dependence of k on c, the rule that $\bar{k} = k$ for $(c'+c'')/2$ is still a good approximation provided $c'-c''$ is small enough.

In their experiments, McBain and Dawson used for calibrating the cells the result of Cohen and Bruins[13] for 0.1 N KCl diffusing into water at 20°, *viz.* 1.448 cm²/day, a value that has been commonly used for this purpose (by the author among others). It is apparent, however, that Cohen and Bruins' measured diffusion constant is an average differing essentially from the average obtained in a Northrop-McBain cell. They allowed decinormal potassium chloride solution to diffuse into a column of water three times the height of the column of solution; the total amount of salt contained in various layers after a suitable length of time was determined, and from this a value of the diffusion constant was computed. To determine the relationship of their average diffusion constant to the differential diffusion constant would require the solution of Eq. (1) with suitable boundary conditions when the k of that equation was a function of c, and this of course is not feasible. Tedious and very approximate calculations show, however, that the average diffusion constant determined in Cohen and Bruins' apparatus will be definitely greater than that measured in a Northrop-McBain cell, both experiments involving the same total range of concentration (0 to 0.1 N). Consequently, the use of Cohen and Bruins' value for calibration will result in too small a value of the cell factor, and thus all subsequent

TABLE III. *KCl at 25°C: $\beta\bar{k}\vartheta = 1.0$.*

t/ϑ	c'	c''	$10^5 \cdot k'$	t/ϑ	c'	c''	$10^5 \cdot k'$
0	0.1000	0.0000	1.845	0.6	0.0774	0.0226	1.834
0.1	.0952	.0048	1.841	.7	.0748	.0252	1.834
.2	.0909	.0091	1.839	.8	.0725	.0275	1.833
.3	.0870	.0130	1.837	0.9	.0703	.0297	1.833
.4	.0835	.0165	1.836	1.0	.0684	.0316	1.832
0.5	0.0803	0.0197	1.835	(∞)	(0.0500)	(0.0500)	(1.832)

[12] Eq. (7) is only valid provided the condition that justifies Eq. (6) is fulfilled, *viz.* that c' and c'' are changing so slowly that the condition obtaining in the diaphragm at all times is practically that for a steady state.

[13] Cohen and Bruins, Zeits. f. physik. Chemie **113**, 157 (1924).

measurements based on this calibration will lead to values of $\bar{k}$ that are too great.

McBain and Dawson found $\bar{k}$ for the diffusion of 0.1 N KCl into water at 25° to be 1.631 cm²/day = 1.888×10^{-5} cm²/sec., nearly three percent greater than the value from Table III. If, however, the result from Table III be used as the calibration, all their values of $\bar{k}$ will be decreased by three percent, and their results for the diffusion of 0.02 N and 0.01 N KCl into water will become 1.899 and 1.929×10^{-5}, in agreement with values of $\bar{k}$ calculated above; moreover, these corrected values now lie on the curve which extrapolates to the limiting value for zero concentration (see Fig. 1). Their results for the diffusion of stronger solutions each into a solution 0.1 N weaker than itself are also subject to a similar correction; these corrected values are indicated by the crossed circles in the figure. The agreement, except for the strongest solution, is satisfactory and is probably within the limits of error of the experiments.

In conclusion, it is suggested that for the calibration of Northrop-McBain cells, the value 1.836×10^{-5} for 0.1 N KCl diffusing into water at 25°C be employed, the duration of the experiment being so adjusted that the final concentration of the upper solution lie near 0.07 N.

The Polarity of Chemical Bonds[1]

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It is shown that polar bonds can be as well considered to be resonating between two covalent states as between one covalent state and an ionic state. The limitation on the number of K electrons in an isolated hydrogen atom does not prevent a hydrogen atom from being bonded at the same time to two other atoms, provided they are sufficiently electronegative. Likewise, a carbon or nitrogen atom, suitably surrounded by electronegative atoms, can hold more than four (bonding) electropairs in its valence shell. It is suggested that Pauling's "magnetic criterion for bond type" does not distinguish between covalent bonds and "ionic bonds," but between covalent bonds of different polarity.

IN the Lewis theory of valence the polarity of a bond was related to the (average) position of the shared electron pair or to the relative attractions of the two bonded atoms for that shared pair. Except for cases involving a change in the number of unpaired electrons, this viewpoint is essentially equivalent to that of Pauling,[2] who speaks of resonance between the "covalent state" and the "ionic state"—the actual electron distribution being intermediate between that for a nonpolar shared electron pair bond and that for two ions:

$$A-B \longleftrightarrow A^+ B^-.$$

The chief purpose of this paper is to point out that it is equally valid to describe a bond having polarity as involving resonance between two covalent states of different polarity—one derived from atomic orbitals having the same principal quantum numbers as those for the valence electrons in the isolated atoms, the other from atomic orbitals one (at least) of which has a higher principal quantum number than for the isolated atom. In the HF molecule, for example, the orbital for the bonding electrons, at the hydrogen end, may be considered to be intermediate in character between an atomic K orbital and an atomic L orbital. Neglecting any contribution of an M atomic state of fluorine to the bond orbital, we may represent this as

$$\underset{K}{\mathrm{H}}\!\!-\!\!\!-\!\!\!-\!\!\underset{L}{\mathrm{F}} \longleftrightarrow \underset{L}{\mathrm{H}}\!\!-\!\!\!-\!\!\!-\!\!\underset{L}{\mathrm{F}}$$

or as

$$\underset{K,L}{\mathrm{H}}\!\!-\!\!\!-\!\!\!-\!\!\!-\!\!\underset{L}{\mathrm{F}}.$$

Resonance between a KL bond orbital and an LL bond orbital should occur to a much greater extent than would be expected from a consideration of the large difference in energy between the atomic K and L states, since an L orbital extends outward from the hydrogen nucleus much farther than does a K orbital and so gives much more overlapping with the fluorine orbital. It seems probable that there is more resonance of this sort than between a state involving a KL bond orbital and an ionic state.

In the $(FHF)^-$ ion, which contains a hydrogen bridge,[3] one would expect the HF bonds to be even more of the LL type. The requirement, deduced from the Pauli principle, that the number of K electrons in an atom cannot exceed two is not applicable to such a structure. There is no experimental or theoretical evidence of which the writer is aware against considering the hydrogen to be bonded at the same time to both fluorine atoms, as represented in any of the following ways:

$$(:\ddot{\mathrm{F}}:\mathrm{H}:\ddot{\mathrm{F}}:)^-, \qquad (\mathrm{F}\!-\!\!-\mathrm{H}\!-\!\!-\mathrm{F})^-,$$

$$\left(\underset{L}{\mathrm{F}}\!\!-\!\!\!-\!\!\!-\!\!\underset{K,L}{\mathrm{H}}\!\!-\!\!\!-\!\!\!-\!\!\underset{L}{\mathrm{F}}\right)^-$$

or $$\left(\underset{L}{\mathrm{F}}\!\!-\!\!\!-\!\!\!-\!\!\underset{K\ L}{\mathrm{H}}\!\!-\!\!\!-\!\!\!-\!\!\underset{L}{\mathrm{F}}\right)^- \longleftrightarrow$$

$$\left(\underset{L}{\mathrm{F}}\!\!-\!\!\!-\!\!\!-\!\!\underset{L\ K}{\mathrm{H}}\!\!-\!\!\!-\!\!\!-\!\!\underset{L}{\mathrm{F}}\right)^-.$$

[1] Some of the material in this paper was included in a paper on "Resonance, Non-Tetrahedral Carbon and Steric Hindrance in Organic Molecules," presented at the Kansas City Meeting of the American Chemical Society, April, 1936.

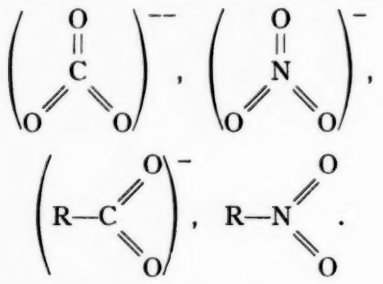
[2] L. Pauling, J. Am. Chem. Soc. **53**, 1367 (1931); **54**, 988 (1932).

[3] M. L. Huggins, unpublished research (1919); see G. N. Lewis, *Valence and the Structure of Atoms and Molecules* (Chemical Catalog Co., New York, 1923), p. 109.

This formulation would seem to be preferable to

$$F^- H^+ F^- \quad \text{or} \quad F^- H{-}F \longleftrightarrow F{-}H\ F^-.$$

Similar reasoning leads to the conclusion that a carbon or nitrogen atom, when bonded to very electronegative atoms, may at times hold more than four electron pairs in its valence shell, some or all of these being bonding pairs occupying orbitals which (at their C or N ends) are intermediate between L and M atomic orbitals:[4]



Since the idea that the atoms in secondary valence complexes are held together by true covalent bonds was first advanced[5] in 1919, much evidence has accumulated in favor of this conception. On the other hand, reasoning from magnetic data (from which may be deduced the number of unpaired electrons) and the requirement that two states of a molecule or ion cannot be combined if they contain different numbers of unpaired electrons, Pauling[6] has concluded that in most cases such a complex belongs to one of two distinct classes—in one of which they are held together by covalent bonds, in the other by "ionic bonds." The ordinary physical and chemical behavior of these substances, however, does not warrant such a distinction. To get around the difficulty, it is suggested that all (or, at least, most) of these complexes are held together by shared electron pairs, the bond orbitals in some instances involving one or more 4*d* orbitals rather than 3*d* (for transition elements in the first long row of the periodic table), as

[4] M. L. Huggins, Phys. Rev. **19**, 346, 354 (1922); J. Am. Chem. Soc. **44**, 1841 (1922); paper on "The Arrangement of Atoms in Organic Molecules," presented at the Eugene Meeting of the A. A. A. S. (1930).

[5] M. L. Huggins, unpublished research (1919); Science, **55**, 459 (1922); J. Phys. Chem. **26**, 601 (1922).

[6] L. Pauling, J. Am. Chem. Soc. **53**, 1367 (1931); L. Pauling and C. D. Coryell, Proc. Nat. Acad. Sci. **22**, 159, 210 (1936).

TABLE I.

	3					4				4	
	d	*d*	*d*	*d*	*d*	*s*	*p*	*p*	*p*	*d*	*d*
Mn^{++}, Fe^{+++}	·	·	·	·	·						
Mn II in MnS_2											
Fe III in $Fe(CN)_6^{---}$, FeAsS	:	:	·	(octahedral bond orbitals)							
Co IV in $CoAs_2$											
Fe III in FeF_6^{---}	·	·	·	·	·	(octahedral bond orbitals)					
Fe III in ferriheme	·	·	·	·	·	(square bond)				(orbs.)	
	·	·	·	·	(square bond orbs.)				·		
Fe^{++}, Co^{+++}	:	·	·	·	·						
Fe II in $Fe(CN)_6^{----}$, FeS_2, ferrohemochromogens, carbon monoxy hemoglobin, oxyhemoglobin	:	:	:	(octahedral bond orbitals)							
Co III in CoAsS											
Ni IV in $NiAs_2$											
Fe II in ferroheme	:	·	·	·	·	(square bond)				(orbs.)	
Ferrohemoglobin	:	·	·	·	(square bond orbs.)				·		
Co II in CoS_2	:	:	:	·	(octahedral bond orbitals)						
Ni III in NiAsS	:	:	:	(octahedral bond orbitals)						·	
Ni II in NiS_2	:	:	:	:	(octahedral bond orbitals)						
	:	:	:	(octahedral bond orbitals)						·	·
Cu II in cupric protoporphyrin	:	:	:	:	·	(square bond)				(orbs.)	
	:	:	:	:	(square bond orbs.)				·		

indicated in Table I. This gives the correct number of unpaired electrons to account for the magnetic data.

Although the $4d$ energy levels are considerably higher than the $3d$ levels, the shift from $3d^2 4s 4p^3$ bond orbitals to $4s 4p^3 4d^2$ bond orbitals is favored by the greater overlapping which the latter can give with the atomic orbitals of the surrounding atoms. The $4s4p^34d^2$ bonds should be more polar than $3d^24s4p^3$ bonds and should predominate for bonds connecting a metal atom to very electronegative atoms. The magnetic data show this to be the case.

For the square cupric, ferrous and ferric complexes, the bond orbitals may be of the $3d4s4p^2$ type, as suggested by Pauling and Coryell for the cupric case, or of the $4s4p^24d$ type. The latter seems to the writer the more probable. The similar beryllium phthalocyanine[7] probably contains $2s2p^23d$ bonds. These would be expected to be very weak, in agreement with the observed reactivity of this compound. Tetrahedral bonds would undoubtedly be much stronger, but they are apparently impossible in view of the rigidity of the plane phthalocyanine structure.

Pauling's original theory also requires modification to account for the existence of CoS_2, NiS_2, NiAsS and other similar compounds containing bivalent cobalt or nickel or trivalent nickel atoms apparently bonded by octahedral bonds to six surrounding electronegative atoms.[8] As in the cupric compounds just discussed, two alternatives are possible (Table I). Magnetic data from NiS_2 might help to decide between them.

[7] R. P. Linstead and J. M. Robertson, J. Chem. Soc. 1736 (1936).

[8] M. L. Huggins, Phys. Rev. **19**, 369 (1922); J. Am. Chem. Soc. **44**, 1841 (1922); L. Pauling and M. L. Huggins, Zeits. f. Krist. **A87**, 205 (1934); M. J. Buerger, Zeits. f. Krist. **A95**, 83 (1936).

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The Determination of the Constants of Harmonic Vibrations

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A general method is developed to find the relations between constants of the potential energy and the frequencies of point systems for harmonic vibrations. Useful formulas are derived (Eqs. (16) and (23)); and matrices required frequently for the solution of problems are tabulated. Relations are also found between the force constants of a molecule with a number of equivalent atoms and the vibration frequencies of an isotopic molecule of a lower degree of symmetry. This also gives the relations between the frequencies of isotopic molecules of different degrees of symmetry.

EXCEPT for the simplest molecules laborious calculations are required to obtain the connection between the potential energy constants and the vibration frequencies of a molecule; this is the case even if we restrict ourselves to the study of harmonic vibrations. The amount of calculation required in each individual case is reduced to a minimum if the *general* treatment is carried out *as far as possible*. This is the object of the present study which is connected with previously published remarks on the subject.[1] A special treatment is necessary for the case where the symmetry of a molecule is lowered when one or more of a number of equivalent atoms are replaced by isotopes.

COMPLEX COORDINATES

As shown already by Brester,[2] the use of complex variables greatly simplifies the necessary transformations of coordinates in the case of any molecule with one threefold or higher proper or improper axis. We start with the Cartesian co-

[1] O. Redlich, Zeits. f. physik. Chemie **B28**, 371 (1935). The product formula derived there was found previously by E. Teller who did not publish it, however.

[2] C. J. Brester, *Kristallsymmetrie und Reststrahlen*, Dissertation (Utrecht, 1923).

ordinates $q_a{}^i$ of the displacements. The index $a=1, 2\cdots n-1, n$ gives the number of the atom; $i=1, 2, 3$ corresponds to the directions x, y and z, respectively. The coordinate system is fixed with respect to the molecule; its origin is at the center of gravity and its axes coincide with the principal axes of inertia. We assume that the (principal) symmetry axis coincides with the z axis. We pass now from the Cartesian to complex coordinates r_c $(c=1, 2, \cdots (3n-1), 3n)$:

$$q_a{}^1=2^{-\frac{1}{2}}(r_a+r_a{}^*); \qquad r_a=2^{-\frac{1}{2}}(q_a{}^1+iq_a{}^2);$$
$$q_a{}^2=i\cdot 2^{-\frac{1}{2}}(-r_a+r_a{}^*); \quad r_{a+n}=r_a{}^*=2^{-\frac{1}{2}}(q_a{}^1-iq_a{}^2);$$
$$q_a{}^3=r_{a+2n}; \qquad r_{a+2n}=q_a{}^3. \tag{1a}$$

The coordinates r_{n+1} to r_{2n} are thus the complex conjugates of r_1 to r_n, the real coordinates r_{2n+1} to r_{3n} are the z components.

If we consider these coordinates as the components of $3n$ dimensional vectors q and r, the coefficients in Eqs. (1a) form the ath step of a unitary matrix U; i.e., the reciprocal matrix U^{-1} is equal to the adjoint $U^\dagger$ (conjugate transposed $\tilde{U}^*$).[3] Hence the transition from q to r can also be represented by

$$q=Ur; \quad r=U^\dagger q; \quad UU^\dagger=E. \tag{1b}$$

We combine the atomic masses M_a to a diagonal matrix with $3n$ rows so that the mass of an atom corresponds to its coordinates. The ath $(a+n)$th and $(a+2n)$th component form a scalar step, namely, the three-rowed unit matrix multiplied by M_a; the steps of U and M are similar. The matrix product MU consists thus of the steps of U multiplied by the corresponding masses. It follows that U and M commute

$$MU=UM; \quad UMU^\dagger=M. \tag{2}$$

We get now for the transformation of the kinetic energy

$$2T=\sum_{a=1,\ i=1}^{a=n,\ i=3} M_a\dot{q}_a{}^{i2}=(M\dot{q},\ \dot{q})$$
$$=(MU\dot{r},\ U\dot{r})=(U^\dagger MU\dot{r},\ \dot{r})=(M\dot{r},\ \dot{r})$$
$$=\sum_{c=1}^{3n} M_c\dot{r}_c{}^*\dot{r}_c. \tag{3}$$

[3] Cf. for example, M. Born and P. Jordan, *Quantenmechanik* (J. Springer, Berlin, 1930); particularly §§6 and 9.

The transformation of the potential energy V and of the matrix A which characterizes it in the Cartesian coordinate system is given by

$$2V=\sum_{a=1,\ b=1,\ i=1,\ j=1}^{a=n,\ b=n,\ i=3,\ j=3} A_{ab}{}^{ij}q_a{}^iq_b{}^j=(Aq,\ q)$$
$$=(U^\dagger AUr,\ r)=(Cr,\ r)=\sum_{c=1,\ d=1}^{3n} C_{cd}r_c{}^*r_d; \tag{4}$$

$$C=U^\dagger AU; \quad C_{cd}=\sum_{abij} U_{ac}{}^{i*}A_{ab}{}^{ij}U_{bd}{}^j; \tag{4a}$$

$$C_{ab}=\tfrac{1}{2}[A_{ab}{}^{11}+A_{ab}{}^{22}+i(-A_{ab}{}^{12}+A_{ab}{}^{21})]$$
$$=C_{ba}{}^*=C^*{}_{a+n,\ b+n}, \tag{4b}$$

$$C_{a,\ b+n}=\tfrac{1}{2}[A_{ab}{}^{11}-A_{ab}{}^{22}+i(A_{ab}{}^{12}+A_{ab}{}^{21})]$$
$$=C^*{}_{b+n,\ a},$$

$$C_{a,\ b+2n}=2^{-\frac{1}{2}}(A_{ab}{}^{13}+iA_{ab}{}^{23})=C^*{}_{b+2n,\ a},$$

$$C_{a+n,\ b+2n}=2^{-\frac{1}{2}}(A_{ab}{}^{13}-iA_{ab}{}^{23})=C^*{}_{b+2n,\ a+n},$$

$$C_{a+2n,\ b+2n}=A_{ab}{}^{33} \qquad =C^*{}_{b+2n,\ a+2n}.$$

The remaining coefficients and a number of further relations may be obtained by interchanging the indices taking into account that $A_{ab}{}^{ij}=A_{ba}{}^{ji}$ or $A=\tilde{A}$. Eqs. (4a) or (4b) show that $C=C^\dagger$, hence C is a hermitian matrix. This result, by the way, follows already from the fact that V is real or that A is real and symmetrical and U is unitary.

Transformation of Coordinates

It has been shown previously[1] that there exists at least one transformation matrix H independent of the atomic masses which transforms the Cartesian coordinates q into "symmetry coordinates" [4] p so that the following conditions are satisfied:

(a) the coordinates p behave the same way as the normal coordinates under the symmetry operations of the undistorted molecule.

[4] Cf. J. B. Howard and E. B. Wilson, Jr., J. Chem. Phys. **2**, 630 (1934). These authors have only stressed condition (*a*) when they introduced the expression "symmetry coordinates"; furthermore, they did not have them independent of the atomic masses. We think that we may restrict their definition in the way indicated here since coordinates which do not satisfy conditions (*b*) and (*c*) are not likely to have much practical importance. See also C. Manneback, Ann. Soc. Sci., Bruxelles **55**, 129 (1935). J. E. Rosenthal and G. M. Murphy, Rev. Mod. Phys. **8**, 317 (1936) call these coordinates "geometrical symmetry coordinates."

(b) H is a step matrix; the elements of each step correspond to the coordinates of equivalent points.

(c) H is orthogonal: $H\tilde{H}=E$.

The same is true for the representation in terms of complex coordinates, the only difference being that the orthogonality condition is replaced by the more general requirement of having H unitary:

(c) $$HH^{\dagger}=E.$$

The following derivations hold formally both if we start with the real variables

$$q=Hp \tag{5a}$$

and the complex variables

$$r=Hp. \tag{5b}$$

H and p and the various quantities that will be introduced obviously have a different meaning in the two cases. A confusion is all the more unlikely since the real and complex coordinates are used in entirely different cases. The complex form is convenient only in the presence of an n-fold axis, $n\geqq 3$ otherwise the real representation should be used.

We note first that the matrix M defined above consists of steps similar to those of the transformation matrix H. Each step is formed by the unit matrix multiplied by the mass of the atom corresponding to it. (Each one of these steps has three times as many rows as there are equivalent points corresponding to it.) Hence H and M commute

$$HM=MH; \qquad HMH^{\dagger}=M. \tag{6}$$

When we pass to symmetry coordinates we obtain similarly to Eq. (3) for the kinetic energy

$$2T=(M\dot{q},\dot{q})=(M\dot{r},\dot{r})$$
$$=(H^{\dagger}MH\dot{p},\dot{p})=(M\dot{p},\dot{p}); \tag{7}$$

hence the matrix M remains in the expression for $2T$ also in the case of the new coordinates.

For the potential energy we obtain

$$2V=(Aq,q)=(Cr,r)=(Bp,p), \tag{8}$$

where either $B=\tilde{H}AH; \quad B=\tilde{B}$ (8a)

or $B=H^{\dagger}CH; \quad B=B^{\dagger}.$ (8b)

Due to the above mentioned symmetry properties of the coordinates p and the invariance of V with respect to the symmetry operations, the components of B with indices referring to coordinates of different types of vibration will vanish. B is hence a step matrix, its steps correspond to the types of vibration. By vibrations of one type we mean vibrations corresponding the same irreducible representation of the group. Different types correspond to different representations.

It is known from Lagrange's equations that

$$(B-\omega^2M)p=0 \tag{9}$$

or $|B-\omega^2M|=0$ if the circular frequency is denoted by ω. As a consequence of the diagonal form of M, ω^2 appears only in the diagonal of the secular determinant.

Useful Formulas

The solution $\omega^2=0$ is contained six times in the $3n$ solutions of the secular determinant, corresponding to the six improper vibrations (the rotations and translations). It is possible to eliminate them quite generally by a method the essentials of which were indicated before.[1] The conservation of angular and linear momenta may be represented by means of the rectangular matrices G and F (6 rows, $3n$ columns) as

$$GMq=GMHp=GHMp=FMp=0;$$
$$G=F\tilde{H}; \tag{10a}$$

or

$$GMr=GMHp=GHMp=FMp=0;$$
$$G=FH.^{\dagger} \tag{10b}$$

In the subsequent discussion we shall let the index 1 indicate that the corresponding vector or the corresponding submatrix refers to the first $3n-6$ coordinates; the index 2 will denote the last 6 coordinates. Accordingly since the rectangular matrices F and G have 6 rows they can only have 2 as first index. Let the original coordinates be so arranged that the determinant of the submatrix G_{22} does not vanish; this is also the case then for F_{22}. This arrangement is always possible (with the exception of trivial cases).

Eqs. (9) and (10) cause the problem to be six times over-determined, i.e., the potential field referred to a coordinate system fixed with respect

to the molecule is already determined by the submatrix B_{11}. The relations between the components of B and F which are necessary for further calculations are found in the following way. If we multiply Eq. (9) with F from the left and take Eqs. (10) into account, then

$$FBp=(F_{21}B_{11}+F_{22}B_{21})p_1 +(F_{21}B_{12}+F_{22}B_{22})p_2=0. \quad (11)$$

Since this equation must be satisfied identically:

$$F_{21}B_{11}+F_{22}B_{21}=F_{21}B_{12}+F_{22}B_{22}=0. \quad (12)$$

It is possible with the help of Eq. (12) to eliminate $B_{12}p_2$ from the system of equations

$$(B_{11}-\omega^2M_{11})p_1+B_{12}p_2=0, \quad (13)$$

$$F_{21}M_{11}p_1+F_{22}M_{22}p_2=0, \quad (14)$$

which we use instead of Eq. (9). We have to take into account for this the fact that $B_{12}=B_{21}^{\dagger}$, a result which follows directly from Eq. (8). Then:

$$\{B_{11}[E+F_{21}^{\dagger}(F_{22}^{-1})^{\dagger}(M_{22})^{-1}F_{22}^{-1}F_{21}M_{11}] -\omega^2M_{11}\}p_1=0 \quad (15)$$

or finally we obtain as the first formula suitable for actual calculation

$$\left|B_{fg}+\sum_{huvw}\frac{M_g}{M_v}B_{fh}F_{uh}{}^{*}F_{wg}(F^{-1})_{vu}{}^{*}(F^{-1})_{vw} -\omega^2M_g\delta_{fg}\right|=0, \quad (16)$$

where f, g, h refer as before to indices from 1 to $3n-6$ and u, v, w to indices from $3n-5$ to $3n$. It is to be noted that we may assume $F_{22}=E$ or

$$(F^{-1})_{vu}{}^{*}=\delta_{vu}; \quad (F^{-1})_{vw}=\delta_{vw}.$$

For we can replace the six equations represented by $FMp=0$ by six others which may be obtained from them by multiplying the rows with constant factors and adding them together. This operation, however, corresponds to a multiplication from the left with any square six-rowed matrix. If we choose for this $(F_{22})^{-1}$, we obtain a matrix which is reduced with reference to the last six columns.

We obtain a second useful formula in the following way. By means of the transformation

$$p_1=s_1+F_{21}^{\dagger}s_2; \quad p_2=F_{22}^{\dagger}s_2 \quad (17)$$

with the help of Eq. (12) we obtain from Eqs. (13) and (14)

$$(B_{11}-\omega^2M_{11})s_1-\omega^2M_{11}F_{21}^{\dagger}s_2=0, \quad (18)$$

$$F_{21}M_{11}s_1+FMF^{\dagger}s_2=0. \quad (19)$$

We introduce now the six-rowed square matrix:

$$S=GMG^{\dagger}=FH^{\dagger}MHF^{\dagger}=FMF^{\dagger}; \quad (20)$$

its invariance follows from Eqs. (6) and (10). The elements denoted by S_{uv} were calculated previously for real coordinates: in the diagonal are the three moments of inertia referred to the three coordinate axes and three times the total mass of the molecule, the other elements are zero. In the complex representation we have for the components S_{uv}

$$S_{11}=S_{22}=\tfrac{1}{2}(I_1+I_2); \quad S_{12}=S_{21}=\tfrac{1}{2}(I_2-I_1) \quad (21)$$

(I_1 and I_2 are moments of inertia with respect to the x and y axes). The other elements have the same value as in the real representation. If the z axis coincides with a threefold or higher order axis, then due to $I_1=I_2$ S is a diagonal matrix in the complex representation as well.

Eliminating s_2 from Eqs. (18) to (20), we obtain

$$(B_{11}-\omega^2M_{11}+\omega^2M_{11}F_{21}^{\dagger}S^{-1}F_{21}M_{11})s_1=0 \quad (22)$$

or as the second useful formula (valid for the complex variable calculation only if the symmetry elements include a threefold or higher order proper or improper axis).

$$\left|B_{fg}-\omega^2M_f\delta_{fg}+\omega^2M_fM_g\sum_v\frac{F_{vf}{}^{*}F_{vg}}{S_{vv}}\right|=0. \quad (23)$$

The first formula (16) is better adapted to the determination of the ω's from the B_{fg}'s, the second one for the inverse procedure. It need not be mentioned specially that both determinants factor out and that each factor corresponds to a special type of vibration.

Isotopic Molecules of Different Degrees of Symmetry

If in a molecule with several equivalent atoms we replace one or more of these by its isotope we obtain a molecule of a lower degree of symmetry (we shall later discuss as an example p-$C_6H_4D_2$).

We shall denote henceforth by original molecule the molecule with a higher degree of symmetry and by substituted molecule the isotopic molecule with a lower degree of symmetry. If we may assume that the potential field is not changed when an atom is replaced by its isotope, we can obtain the frequencies of the substituted molecule in terms of the constants of the potential energy of the original one. The number of constants is thus smaller than in the case of a non-isotopic molecule with the same configuration (for example, p-$C_6H_4Cl_2$). General formulas may be set up for the connection between the frequencies of the substituted molecule with the constants of the potential energy of the original molecule.

In the subsequent discussion we shall use the same notation as before for the substituted molecule; matrices referring to the original one will be written in Gothic script, e.g., $\mathfrak{H}$, $\mathfrak{F}$, $\mathfrak{B}$. Let $\mathfrak{p}$ denote the coordinates of the displacements obtained by performing on the Cartesian or complex coordinates of both molecules a transformation $\mathfrak{H}$, which satisfies the rules given above for the original molecule. The $\mathfrak{p}$'s are thus symmetry coordinates for the original but not for the substituted molecule. The connection between the p's and the $\mathfrak{p}$'s is given by

$$q=Hp=\mathfrak{H}\mathfrak{p};\quad \text{or}\quad r=Hp=\mathfrak{H}\mathfrak{p};\quad p=H^{\dagger}\mathfrak{H}\mathfrak{p}. \tag{24}$$

The product $H^{\dagger}\mathfrak{H}$ is unitary but its steps obviously do not correspond to points equivalent with respect to the symmetry elements of the substituted molecule; they are larger and correspond to points equivalent with respect to the symmetry elements of the original molecule. For the kinetic energy we obtain

$$\begin{aligned}2T&=(M\dot{p},\dot{p})=(\mathfrak{H}^{\dagger}HMH^{\dagger}\mathfrak{H}\dot{\mathfrak{p}},\dot{\mathfrak{p}})\\&=(\mathfrak{H}^{\dagger}M\mathfrak{H}\dot{\mathfrak{p}},\dot{\mathfrak{p}})=(N\dot{\mathfrak{p}},\dot{\mathfrak{p}});\quad N=\mathfrak{H}^{\dagger}M\mathfrak{H}.\end{aligned} \tag{25}$$

The Hermitian matrix N or to be more accurate its deviation from M, represents a measure of the difference in symmetry between the two molecules. The potential energy is given by

$$\begin{aligned}2V&=(Bp,p)=(\mathfrak{H}^{\dagger}HBH^{\dagger}\mathfrak{H}\mathfrak{p},\mathfrak{p})\\&=(\mathfrak{B}\mathfrak{p},\mathfrak{p});\quad \mathfrak{B}=\mathfrak{H}^{\dagger}HBH^{\dagger}\mathfrak{H}.\end{aligned} \tag{26}$$

By analogy to Eq. (9) we obtain from Eqs. (25) and (26)

$$(\mathfrak{B}-\omega^2N)\mathfrak{p}=0. \tag{27}$$

To eliminate the improper vibrations we obtain first the connection between the matrices F and $\mathfrak{F}$ of the angular and linear momenta expressed in terms of the symmetry coordinates of both molecules. We make use of the fact that the matrix G (Eq. (10)) which depends only on the atomic distances is the same for both molecules. Hence

$$G=FH^{\dagger}=\mathfrak{F}\mathfrak{H}^{\dagger};\quad F=\mathfrak{F}\mathfrak{H}^{\dagger}H; \tag{28}$$

the expressions for the momenta take on the form

$$\begin{aligned}FMp&=FMH^{\dagger}\mathfrak{H}\mathfrak{p}=FH^{\dagger}M\mathfrak{H}\mathfrak{p}\\&=\mathfrak{F}\mathfrak{H}^{\dagger}M\mathfrak{H}\mathfrak{p}=\mathfrak{F}N\mathfrak{p}=Q\mathfrak{p}=0;\quad Q=\mathfrak{F}N.\end{aligned} \tag{29}$$

The six-rowed matrix S defined by Eq. (20) is

$$\begin{aligned}S=FMF^{\dagger}&=\mathfrak{F}\mathfrak{H}^{\dagger}HMH^{\dagger}\mathfrak{H}\mathfrak{F}^{\dagger}\\&=\mathfrak{F}\mathfrak{H}^{\dagger}M\mathfrak{H}\mathfrak{F}^{\dagger}=\mathfrak{F}N\mathfrak{F}^{\dagger}.\end{aligned} \tag{30}$$

By a calculation analogous to the transition from Eqs. (9) and (10) to Eqs. (15) and (22) we find

$$\begin{aligned}&\mathfrak{B}_{11}[E+\mathfrak{F}_{21}{}^{\dagger}(\mathfrak{F}_{22}{}^{-1})^{\dagger}Q_{22}{}^{-1}Q_{21}]\\&\qquad-\omega^2(N_{11}-N_{12}Q_{22}{}^{-1}Q_{21})\mathfrak{p}_1=0;\end{aligned} \tag{31}$$

$$(\mathfrak{B}_{11}-\omega^2N_{11}+\omega^2Q_{21}{}^{\dagger}S^{-1}Q_{21})\mathfrak{s}_1=0; \tag{32}$$

where $\mathfrak{s}_1$, is defined analogously to s, in Eq. (17). These equations give us the connection between the frequencies ω of the substituted molecule and the constants $\mathfrak{B}$ of the potential energy of the original molecule in a form suitable for further calculation.

We can also eliminate the submatrices $\mathfrak{B}_{12}$, $\mathfrak{B}_{21}$, and $\mathfrak{B}_{22}$ from $B=H^{\dagger}\mathfrak{H}\mathfrak{B}\mathfrak{H}^{\dagger}H$ with the help of the equation analogous to Eq. (12); the value obtained for B_{11} can be substituted directly in Eqs. (15) or (22).

The corresponding determinants break up into factors which correspond to the types of vibration of the substituted molecule.

If a symmetry type contains no improper vibrations, Eqs. (31) and (32) become identical with Eq. (27). We shall derive as an example for this simple case the totally symmetrical vibrations A_1 of p-dideuterobenzene, a result we used before without deriving it then.[5] The indices 1 to

[5] O. Redlich, W. Stricks, Mh. Chem. **68**, 374 (1936); also Sitz. Ber. Akad. Wiss. Wien (II*b*) **145**, 594 (1936). We should like to point out that the zero determinant given there differs only formally and not actually from Wilson's result for the type of symmetry $E_g{}^+$. The determinants may be transformed into one another if $d=H/2$ and $D=k-H\eta^2/4$. We are grateful to Dr. Wilson for pointing it out to us. The numerical results remain unchanged.

6 of the Cartesian coordinates refer to C (mass M_1); 7 and 10 to D (mass M_2''); 8, 9, 11, and 12 to H (mass M_2'). The indices of p and $\mathfrak{p}$ are chosen with regard to Wilson's numbering of the vibrations. No further explanation should be necessary for the following scheme of coefficients which contain the necessary parts of H, $\mathfrak{H}$ and N.

COMPONENTS OF H AND $\mathfrak{H}$

	q	$p_1(p_2)$	$p_6(p_7)$	$p_8(p_9)$	$\mathfrak{p}_1(\mathfrak{p}_2)$	$\mathfrak{p}_6(\mathfrak{p}_7)$	$\mathfrak{p}_8(\mathfrak{p}_9)$
$M_1(M_2'')$	$x_1(x_7)$	$1/\sqrt{2}$	0	0	$1/\sqrt{6}$	$1/\sqrt{3}$	0
	$x_4(x_{10})$	$-1/\sqrt{2}$	0	0	$-1/\sqrt{6}$	$-1/\sqrt{3}$	0
$M_1(M_2')$	$x_2(x_8)$	0	1/4	$\sqrt{3}/4$	$1/2\sqrt{6}$	$-1/4\sqrt{3}$	$\sqrt{3}/4$
	$x_3(x_9)$	0	$-1/4$	$-\sqrt{3}/4$	$-1/2\sqrt{6}$	$1/4\sqrt{3}$	$-\sqrt{3}/4$
	$x_5(x_{11})$	0	$-1/4$	$-\sqrt{3}/4$	$-1/2\sqrt{6}$	$1/4\sqrt{3}$	$-\sqrt{3}/4$
	$x_6(x_{12})$	0	1/4	$\sqrt{3}/4$	$1/2\sqrt{6}$	$-1/4\sqrt{3}$	$\sqrt{3}/4$
	$y_2(y_8)$	0	$\sqrt{3}/4$	$-1/4$	$1/2\sqrt{2}$	$-1/4$	$-1/4$
	$y_3(y_9)$	0	$\sqrt{3}/4$	$-1/4$	$1/2\sqrt{2}$	$-1/4$	$-1/4$
	$y_5(y_{11})$	0	$-\sqrt{3}/4$	1/4	$-1/2\sqrt{2}$	1/4	1/4
	$y_6(y_{12})$	0	$-\sqrt{3}/4$	1/4	$-1/2\sqrt{2}$	1/4	1/4

COMPONENTS OF N

$$N_{11}=N_{66}=N_{88}=M_1; \quad N_{99}=M_2'; \quad N_{22}=r=(M_2''+2M_2')/3;$$
$$N_{27}=N_{72}=s=(M_2''-M_2')\cdot\sqrt{2}/3; \quad N_{77}=t=(2M_2''+M_2')/3;$$

the other components are zero.

With these coefficients of N we obtain the zero determinant corresponding to Eq. (27) given in the previous reference.

EVALUATION OF THE DETERMINANTS

With the abbreviations

$$K_{11}=M_{11}^{-1}+F_{21}\dagger(F_{22}^{-1})\dagger M_{22}^{-1}F_{22}^{-1}F_{21}; \quad (33)$$

$$L_{11}=M_{11}-M_{11}F_{21}\dagger S^{-1}F_{21}M_{11}, \quad (34)$$

Eqs. (15) and (22) take the form[6]

$$(B_{11}K_{11}-\omega^2E)M_{11}p_1=0; \qquad (B_{11}-\omega^2L_{11})s_1=0. \quad (35)$$

The secular determinants can be written:

$$\sum_{j=0}^{3n-6}\psi_j(-\omega^2)^{3n-6-j}=0. \quad (36)$$

Ψ_j/Ψ_0 represents on one hand the sum of the products of the jth order of the squares of the frequencies obtained by writing the $\binom{3n-6}{j}$ combinations of the jth class without repeating any factors. On the other hand Ψ_j may also be represented:

(a) as the sum of the $\binom{3n-6}{j}$ principal minors of the jth order of the determinant

$$|B_{11}K_{11}|=|\sum_h B_{fh}K_{hg}|.$$

(b) or as the sum of the $\binom{3n-6}{j}^2$ products of the minors of the jth order which belong to corresponding elements of the determinants $|B_{11}|$ and $|K_{11}|$.

(c) or as the sum of the $\binom{3n-6}{j}^2$ products of the minors of the $(3n-6-j)$th order of $|L_{11}|$ with the corresponding minors of the jth order of $|B_{11}|$.

The same results hold also for the treatment of Eqs. (31) and (32), the meaning of K_{11} and L_{11} being changed, however. Naturally the reasoning can also be applied separately to each type of vibration.

If we have the frequencies ω_f' and ω_f'' of two isotopic molecules we can make use of simpler relations between force constants and frequencies, which might sometimes be valuable for the determination of the force constants. We start from Eq. (9) from which the improper vibrations have not yet been eliminated. The coefficients ϕ_k of the secular equation

$$\sum_{k=0}^{3n}\phi_k(\omega^2)^{3n-k}=0$$

are again on one hand equal to the sum of the products of the kth order of the squares of the frequencies, and on the other hand equal to the sum of the principal minors of kth order of the determinant $|BM^{-1}|=|B_{ab}/M_b|$. In particular,

[6] It should be noted that $K_{11}L_{11}=E$.

we obtain[7]

$$\sum_{f=1}^{3n-6}\omega_f'^2=\sum_{a=1}^{3n}\frac{B_{aa}}{M_a'};\quad \sum_{f=1}^{3n-6}\omega_f''^2=\sum_{a=1}^{3n}\frac{B_{aa}}{M_a''};$$

$$\sum_{f=1}^{3n-6}\Delta\omega_f^2=\sum_{a=1}^{3n}B_{aa}\Delta\frac{1}{M_a}. \quad (37)$$

The second coefficient of the secular equation gives

$$\sum_{f\neq g}^{3n-6}\omega_f^2\omega_g^2=\sum_{ab}^{3n}\frac{B_{aa}B_{bb}-B_{ab}^2}{M_aM_b}; \quad (38)$$

in both summations each pair of indices is to appear only once. The last two relations give

$$\sum\omega_f^4=(\sum\omega_f^2)^2-2\sum_{f\neq g}\omega_f^2\omega_g^2=\left(\sum_a\frac{B_{aa}}{M_a}\right)^2$$

$$-2\sum_{ab}\frac{B_{aa}B_{bb}-B_{ab}^2}{M_aM_b}=\sum_a\frac{B_{aa}^2}{M_a^2}+2\sum_{a\neq b}\frac{B_{ab}^2}{M_aM_b} \quad (39)$$

or if $a=b$ is also permitted and each combination of indices may appear twice (for a, b and b, a):

$$\sum_f\omega_f^4=\sum_{ab}\frac{B_{ab}^2}{M_aM_b};\quad \sum_f\Delta\omega_f^4=\sum_{ab}B_{ab}^2\Delta\frac{1}{M_aM_b}. \quad (40)$$

If only one kind of atom c is replaced by its isotope these relations are further simplified to

$$\sum_{f=1}^{3n-6}\Delta\omega_f^2=\Delta\frac{1}{M_c}\sum_c B_{cc};$$

$$\sum_{f=1}^{3n-6}\Delta\omega_f^4=2\Delta\frac{1}{M_c}\sum_{ac}\frac{B_{ac}^2}{M_a}+\left(\Delta\frac{1}{M_c}\right)^2\sum_c B_{cc}^2. \quad (41)$$

In these equations the index c refers to coordinates of atoms replaced by their isotopes; the index a takes on all values from 1 to $3n$.

We can obviously proceed to higher powers in similar fashion. These relations are of particular advantage for treating types of vibration which do not include improper vibrations.

Tables for Some of the Transformation Matrices

As mentioned before, the quantities H given in Eqs. (5) are step matrices; each step corresponds to a set of equivalent points. In the appendix the elements of these submatrices are tabulated for some of the more important point groups.

The tables are headed by the symbol of the point group and (in parentheses) the coordinates of the equilibrium configuration. The left (upper) part of each table contains the elements of the submatrix of $m^{\frac{1}{2}}H$ where m gives the number of equivalent points in question. On the left are given the indices of the Cartesian coordinates q (real), or r (complex). The indices of the first column refer to the $x-$ or (in the complex case) to the $2^{-\frac{1}{2}}(x+iy)$ coordinates of the m atoms, the indices of the second column to the $y-$ or the $2^{-\frac{1}{2}}(x-iy)$-coordinates; the third column corresponds to the z coordinates. The sequence of the m atoms may be seen from the heading of the table. The upper three rows contain the indices of the symmetry coordinates p. The scheme of elements of $m^{\frac{1}{2}}H$ belongs to the first column of the indices of q (or r) and to the first row of the indices of p as well as to the second column and second row and the third column and third row. For the sake of clarity we give in detail the submatrix H for C_2 which may be compared with the corresponding table

$1/\sqrt{2}$	0	0	$1/\sqrt{2}$	0	0
$-1/\sqrt{2}$	0	0	$1/\sqrt{2}$	0	0
0	$1/\sqrt{2}$	0	0	$1/\sqrt{2}$	0
0	$-1/\sqrt{2}$	0	0	$1/\sqrt{2}$	0
0	0	$1/\sqrt{2}$	0	0	$1/\sqrt{2}$
0	0	$1/\sqrt{2}$	0	0	$-1/\sqrt{2}$

The right (lower) part of each table contains the elements of the submatrices of $m^{-\frac{1}{2}}F$; the columns correspond in order to the symmetry coordinates p in the same numbering as given in the upper three rows of the tables for $m^{\frac{1}{2}}H$. The upper row gives the symmetry types in Placzek's notation;[8] then come the components of the angular momentum and finally the components of the linear momentum. The vacancies correspond to zeros.

For points situated on a symmetry element we use only those operations valid for the general type of points which do not refer to this particular element.

The matrices H may be developed from Brester's[2] results. In some special cases they have also been given by other authors (Wilson, Manneback, and others). Their explicit tabulation seemed to us to be of interest, since reference to such tables would save a great deal of work and also because Brester's paper is rather inaccessible.

The calculation of a molecular model proceeds

[7] H. Tompa, Nature **137**, 951 (1936). The quantity in the second equation there should be A_{ab}^2 instead of A_{ab}.

[8] G. Placzek, *Handbuch der Radiologie*, second edition, Vol. 6.

hence in the following way. We select a system of coordinates with its origin at the center of gravity and its axes along the principal axes of inertia. The z axis is taken to be along the principal axis of symmetry (if it exists). The x components of the Cartesian coordinates have the indices 1 to n, the y components the indices $n+1$ to $2n$ and the z components the indices $2n+1$ to $3n$. The sequence of the atoms at equivalent points is to be seen from the headings of the table. With the help of the tables for $m^{-\frac{1}{2}}F$ we set up the expressions for the conservation of momenta. We select six of the symmetry coordinates p so that the determinant of the corresponding submatrix $|F_{22}| \neq 0$. In general there is still some arbitrariness left, however, only within a particular type of symmetry. The connection between the constants B_{ab} of the potential energy and the frequencies of vibration is given for each symmetry type by Eqs. (15) or (22). The meaning of particular symmetry coordinates and hence of particular force constants follows from a discussion of the transformation H. The determination from Eqs. (8) of the force constants referred to the Cartesian coordinates will be in general superfluous.

We believe that with this method of calculation the amount of labor necessary for the solution of each particular problem will be reduced to a minimum.

Appendix. Tables for the Matrices $m^{\frac{1}{2}}H$ and $m^{-\frac{1}{2}}F$

C_1 (a, b, c)

q \ p	1	2	3
1	1		
2		1	
3			1

	c	$-b$
$-c$		a
b	$-a$	
1		
	1	
		1

C_2 $(a, b, c; -a, -b, c)$

q \ p	4	1
	5	2
	3	6
1 3 5	1	1
2 4 6	1	-1

A			B	
			c	$-b$
b	$-a$		$-c$	a
			1	
				1
		1		

C_i $(a, b, c; -a, -b, -c)$

q \ p	4	1
	5	2
	6	3
1 3 5	1	1
2 4 6	1	-1

g			u
	c	$-b$	
$-c$		a	
b	$-a$		
			1
			1
			1

C_s $(a, b, c; a, b, -c)$

q \ p	1	4
	2	5
	6	3
1 3 5	1	1
2 4 6	1	-1

A'			A''	
			c	$-b$
b	$-a$		$-c$	a
1				
	1			
				1

C_{2h} $(a, b, c; -a, -b, c; a, b, -c; -a, -b, -c)$

q \ p	10	4	1	7
	11	5	2	8
	9	3	6	12
1 5 9	1	1	1	1
2 6 10	1	1	-1	-1
3 7 11	1	-1	1	-1
4 8 12	1	-1	-1	1

A_g		B_g		A_u	B_u
		c	$-b$		
b	$-a$	$-c$	a		
					1
					1
				1	

C_{2v} $(a, b, c; -a, b, c; a, -b, c; -a, -b, c)$

q \ p	7	4	1	10
	11	2	5	8
	3	12	9	6
1 5 9	1	1	1	1
2 6 10	1	1	-1	-1
3 7 11	1	-1	1	-1
4 8 12	1	-1	-1	1

A_1	A_2		B_1		B_2	
					c	$-b$
	b	$-a$	$-c$	a		
			1			
					1	
1						

V $(a, b, c; a, -b, -c; -a, b, -c; -a, -b, c)$

q \ p			10	1	4	7
			8	5	2	11
			6	9	12	3
1	5	9	1	1	1	1
2	6	10	1	1	−1	−1
3	7	11	1	−1	1	−1
4	8	12	1	−1	−1	1

A	B_1	B_2	B_3
			$c \quad -b$
		$-c \qquad a$	
	$b \quad -a$		
			1
		1	
	1		

V_h $(a, b, c; a, -b, -c; -a, b, -c; -a, -b, c; -a, -b, -c; -a, b, c; a, -b, c; a, b, -c)$

q \ p			22	10	13	1	16	4	19	7
			20	8	17	5	14	2	23	11
			18	6	21	9	24	12	15	3
1	9	17	1	1	1	1	1	1	1	1
2	10	18	1	1	1	1	−1	−1	−1	−1
3	11	19	1	1	−1	−1	1	1	−1	−1
4	12	20	1	1	−1	−1	−1	−1	1	1
5	13	21	1	−1	1	−1	1	−1	1	−1
6	14	22	1	−1	1	−1	−1	1	−1	1
7	15	23	1	−1	−1	1	1	−1	−1	1
8	16	24	1	−1	−1	1	−1	1	1	−1

A_g	B_{1g}	B_{2g}	B_{3g}	A_u	B_{1u}	B_{2u}	B_{3u}
			$c \quad -b$				
		$-c \qquad a$					
	$b \quad -a$						
							1
						1	
					1		

C_3 $(a, a^*, c; a\epsilon, a^*\epsilon^2, c; a\epsilon^2, a^*\epsilon, c)$ $\qquad \epsilon = e^{2\pi i/3}$

r \ p			4	1	7
			8	5	2
			3	9	6
1	4	7	1	1	1
2	5	8	1	ϵ	ϵ^2
3	6	9	1	ϵ^2	ϵ

A	E	E
		$c \quad -a^*$
	$-c \qquad a$	
$a^* \quad -a$		
	1	
1		1

C_4 $(a, a^*, c; ia, -ia^*, c; -a, -a^*, c; -ia, ia^*, c)$

r \ p			7	1	10	4
			11	5	8	2
			3	12	6	9
1	5	9	1	1	1	1
2	6	10	1	i	−1	$-i$
3	7	11	1	−1	1	−1
4	8	12	1	$-i$	−1	i

A	B	E	E
			$c \quad -a^*$
		$-c \qquad a$	
$a^* \quad -a$			
		1	
1			1

S_4 $(a, a^*, c; ia, -ia^*, -c; -a, -a^*, c; -ia, ia^*, -c)$

r \ p			7	1	10	4
			11	5	8	2
			6	9	3	12
1	5	9	1	1	1	1
2	6	10	1	i	−1	$-i$
3	7	11	1	−1	1	−1
4	8	12	1	$-i$	−1	i

A	B	E	E
		$c \quad -a^*$	
			$-c \qquad a$
$a^* \quad -a$			
		1	
	1		1

C_{3h} $(a, a^*, c; a\epsilon, a^*\epsilon^2, c; a\epsilon^2, a^*\epsilon, c; a, a^*, -c; a\epsilon, a^*, \epsilon^2 - c; a\epsilon^2, a^*\epsilon, -c)$ $\epsilon = e^{2\pi i/3}$

r \ p	7	1	10	13	4	16
	11	8	2	17	14	5
	6	18	15	3	12	9
1 7 13	1	1	1	1	1	1
2 8 14	1	ϵ	ϵ^2	1	ϵ	ϵ^2
3 9 15	1	ϵ^2	ϵ	1	ϵ^2	ϵ
4 10 16	1	1	1	−1	−1	−1
5 11 17	1	ϵ	ϵ^2	−1	$-\epsilon$	$-\epsilon^2$
6 12 18	1	ϵ^2	ϵ	−1	$-\epsilon^2$	$-\epsilon$

A'	A''	E'	E'	E''	E''
					$c\ -a^*$
				$-c$ a	
$a^*\ -a$					
		1			
			1		
	1				

C_6 $(a, a^*, c; a\epsilon, a^*\epsilon^5, c; a\epsilon^2, a^*\epsilon^4, c; -a, -a^*, c; a\epsilon^4, a^*\epsilon^2, c; a\epsilon^5, a^*\epsilon, c)$ $\epsilon = e^{2\pi i/6}$

r \ p	13	1	16	7	4	10
	17	8	5	11	14	2
	3	18	9	6	12	15
1 7 13	1	1	1	1	1	1
2 8 14	1	ϵ	ϵ^2	ϵ^3	ϵ^4	ϵ^5
3 9 15	1	ϵ^2	ϵ^4	1	ϵ^2	ϵ^4
4 10 16	1	ϵ^3	1	ϵ^3	1	ϵ^3
5 11 17	1	ϵ^4	ϵ^2	1	ϵ^4	ϵ^2
6 12 18	1	ϵ^5	ϵ^4	ϵ^3	ϵ^2	ϵ

A	B	E^+	E^+	E^-	E^-
					$c\ -a^*$
				$-c$ a	
$a^*\ -a$					
				1	
					1
1					

S_6 $(a, a^*, c; a\epsilon, a^*\epsilon^5, -c; a\epsilon^2, a^*\epsilon^4, c; -a, -a^*, -c; a\epsilon^4, a^*\epsilon^2, c; a\epsilon^5, a^*\epsilon, -c)$ $\epsilon = e^{2\pi i/6}$

r \ p	13	1	16	7	4	10
	17	8	5	11	14	2
	6	12	15	3	18	9
1 7 13	1	1	1	1	1	1
2 8 14	1	ϵ	ϵ^2	ϵ^3	ϵ^4	ϵ^5
3 9 15	1	ϵ^2	ϵ^4	1	ϵ^2	ϵ^4
4 10 16	1	ϵ^3	1	ϵ^3	1	ϵ^3
5 11 17	1	ϵ^4	ϵ^2	1	ϵ^4	ϵ^2
6 12 18	1	ϵ^5	ϵ^4	ϵ^3	ϵ^2	ϵ

A_g	A_u	E_g	E_g	E_u	E_u
			$c\ -a^*$		
		$-c$ a			
$a^*\ -a$					
				1	
	1				1

The Heat Capacities of Benzene, Methyl Alcohol and Glycerol at Very Low Temperatures[1]

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The design and operation of a low temperature vacuum calorimeter which is internally cooled from 13° to 2°K is described. The principle employed is that of adiabatically expanding cooled helium gas from a small pressure chamber, located inside the calorimeter can. The heat capacities of crystalline benzene and methyl alcohol and crystalline and glassy glycerol have been measured down to 3°K. New values of the entropies of these substances at various temperatures have been calculated. Below 9°K the heat capacity of glassy glycerol is 100 percent larger than that of crystalline glycerol. The glassy form apparently has 4.64 units of entropy at the absolute zero.

INTRODUCTION

THE demonstrations by Simon and Ahlberg[5, 6] that a thermally isolated apparatus could be effectively cooled from "hydrogen" to "helium temperatures" by the free adiabatic expansion of cold helium gas from a small pressure chamber at once suggested that the inclusion of a simple auxiliary appliance in the familiar type of low temperature vacuum calorimeter would make it possible to extend heat capacity measurements to within several degrees of the absolute zero even when liquid hydrogen was available only in moderate quantities. In connection with the development of such a calorimeter it seemed worth while to make an experimental investigation of the very low temperature heat capacities of a few organic compounds which form crystal lattices of the molecular type.

The experimental investigation of the low temperature thermal behavior of the crystalline state has been confined, for the most part, to substances forming crystal lattices of the monatomic particle type. The heat capacity of lattices composed of large molecules has, in most instances, simply been inferred from measurements at relatively high temperatures and from what was known about simpler types of structures. But in many organic substances the vibrations of the atomic nuclei or groups of nuclei within the individual molecules begin to be appreciable factors in the total heat capacity even at "hydrogen temperatures" and at somewhat higher temperatures they become the most conspicuous factors, effectively obscuring the fine gradation in the heat capacity arising from compressional and torsional vibrations of the Debye type in the crystal lattice. It is often, therefore, only at "helium temperatures" that the observed heat capacities may be considered to give a simple, unconfused picture of the thermal behavior of a molecular crystal lattice. With an exact knowledge of the fraction of the total heat capacity which arises from lattice vibrations, it becomes possible easily to compute an experimental value for the heat capacity of the internal vibrations in the molecules. The latter information is often of great value in the interpretation of spectroscopic frequencies.

APPARATUS

General description

The calorimeter was designed primarily for measurements of heat capacity between 2° and 20°K but arrangements were also provided for continuing the measurements up to 100°K. Apart from the helium liquefaction device, the plan and operation of the calorimeter was, in principle, similar to the types of calorimeters developed by Nernst, Simon, Giauque and others. By confining the operating range of the calorimeter to temperatures below 100°K it was possible to dispense with the bulky, massive radia-

[1] A portion of the contents of this paper, including a description of the calorimeter and the measurements on benzene, was presented at the 88th Meeting of the American Chemical Society in Cleveland, O., September, 1934.
[2] Present address: Universal Oil Products Company, Chicago, Ill.
[3] Grafflin Fellow, Johns Hopkins University, 1933–35.
[4] Hormel Foundation Fellow in Chemistry, 1930–34.
[5] F. Simon, Zeits. f. ges. Kälte-Ind. **39**, 89 (1932).
[6] Simon and Ahlberg, Zeits. f. Physik **81**, 816 (1933).

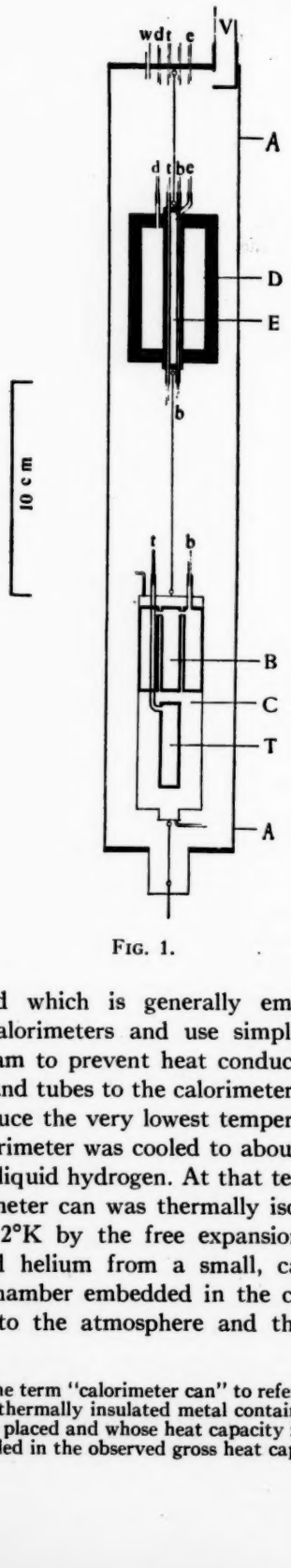

FIG. 1.

tion shield which is generally employed in vacuum calorimeters and use simply a small thermal dam to prevent heat conduction along the wires and tubes to the calorimeter can.[7]

To produce the very lowest temperatures the whole calorimeter was cooled to about 13°K by the use of liquid hydrogen. At that temperature the calorimeter can was thermally isolated and cooled to 2°K by the free expansion of cold, compressed helium from a small, capsule-like pressure chamber embedded in the calorimeter can, first to the atmosphere and then into a vacuum.

[7] We use the term "calorimeter can" to refer specifically to the light, thermally insulated metal container in which the sample is placed and whose heat capacity is, of course, always included in the observed gross heat capacities.

Between 2° and 20°K, absolute temperatures were determined by the use of a constant volume helium gas thermometer whose bulb was imbedded in the material in the calorimeter can. Temperature intervals were measured with great accuracy by a high resistance constantan wire coil which was wound on the outside of the calorimeter can and which served both as a resistance thermometer and as the heating element. The resistance thermometer was calibrated against the gas thermometer at many temperatures during the course of every series of heat capacity measurements. Thermocouples were used for temperature measurements above 20°K.

Fig. 1 shows the vacuum compartment of the calorimeter and its contents. The liquid hydrogen cryostat (not shown) consisted of a deep glass Dewar vessel enclosed in a tight brass can which was arranged to permit boiling of the hydrogen under reduced pressure. The entire hydrogen cryostat was suspended in a deep, nickel silver vacuum container of liquid nitrogen.

Referring to Fig. 1: *A* is the vacuum compartment which was entirely immersed in liquid hydrogen when the calorimeter was in operation at low temperatures; *C* is the calorimeter can in which the materials to be investigated were sealed; *B* is the helium liquefier; *D* is an auxiliary helium liquefier and reservoir which served as a thermal dam for the control of heat leakage along the wires and tubes leading to the calorimeter can below; *T* is the bulb of the standard gas thermometer and *E* is the bulb of an auxiliary gas thermometer in the dam. To isolate *C* and *D* thermally from the liquid hydrogen bath the vacuum compartment could be evacuated to 10^{-6} mm of mercury through the tube *V*.

The helium liquefying chambers, *B* and *D* were in communication with the outside of the cryostat through small German silver tubes, indicated by *b* and *d*. The gas thermometer bulbs, *T* and *E*, connected with their respective manometers through German silver capillary tubes, indicated by *t* and *e*. All of these tubes were coiled together in a helical spiral for several turns in the space between *D* and the top of the vacuum compartment. Between *D* and *C* the tubes *b* and *t* had a length of about one meter, being coiled in a helix of ten turns. By these means the tubes

were given great length in a small space, thereby greatly reducing heat leakage along them. All of the electrical leads to the vacuum compartment were conducted inside a small copper tube, *w*, through the hydrogen bath to the outside of the cryostat where they emerged through a vacuum tight, plastic seal.

Calorimeter can

The calorimeter can, *C*, was a cylindrical container made from pure silver tube and sheet of 0.3 mm thickness. The can was 10 cm high, 3.3 cm in diameter and held about 60 cc of material. Six radial fins of silver foil, extending from the wall towards the center, were soldered into the can to promote rapid conduction of heat through the sample. For the same purpose the can was filled with a low pressure of helium gas at the time a sample was sealed in. Ordinary 60 Sn – 40 Pb solder was used in the construction of the can. Suspended inside the can was the small pressure chamber, *B*, in which helium was liquefied and subsequently boiled under reduced pressure. The chamber consisted of several short, interconnected sections of silver tube of 1 mm wall thickness and had a total volume of 6 cc. The German silver tube, *b*, used for the admission and expansion of helium had an o.d. of 1.6 mm and an i.d. of 1 mm.[8]

The bulb, *T*, of the standard gas thermometer was permanently suspended in the center of the calorimeter can. It was made from a section of stout silver tube and had a volume of 2 cc. Leading from the bulb to the top of the cryostat was a continuous piece of German silver capillary tubing, *t*, which had an internal diameter of 0.22 mm.

Thermal dam

The protective helium reservoir, *D*, was a massive, hollow copper cylinder suspended from the top of the vacuum compartment by a stout silk fishline. The electrical wires leading to the calorimeter can below were wound around and cemented to the cylinder while the tubes *b* and *t* passed through the cylinder. When partially filled with liquid helium this dam provided sufficient thermal insulation for the calorimeter can below to permit the latter to be held at 1.5°K for several hours. For measurements above the boiling point of helium the cylinder contained a sufficient mass of copper to enable it to serve as a thermal dam simply by virtue of the heat capacity of the metal. By means of a heating coil wound on its outside, the cylinder could be brought to approximately the temperature of the calorimeter can below. Inside the dam was a copper cylinder, *E*, which served as the bulb of a helium gas thermometer used for control purposes at the lowest temperatures. It was connected by a German silver tube, *e* (0.4 mm i.d.), to an ordinary Bourdon type vacuum gauge on the outside of the cryostat.[9] This thermometer was filled with helium gas to a pressure of one atmosphere when the system was at 298°K. At very low temperatures this simple arrangement functioned well as a moderately sensitive thermometer.

Cooling procedure

To cool the calorimeter to "helium temperatures" compressed helium from a commercial storage cylinder was allowed to flow, first, through a high pressure purifying system, and then into the pressure chambers, *B* and *D*, while the latter were in contact with liquid hydrogen boiling under reduced pressure. Thermal contact between *B* and *C* and the boiling hydrogen, which surrounded the vacuum compartment, was established by admitting helium gas to the vacuum compartment to a pressure of 1 cm (at 298°K). After the compressed helium had cooled to the lowest temperature attainable with hydrogen (12° to 14°K in practice), the dam, *D*, and the calorimeter can, *C*, were thermally isolated by pumping the exchange gas completely out of the vacuum compartment. The cold compressed helium in the two pressure chambers was then released slowly to the atmosphere simply by loosening the coupling nuts by which the feed lines were attached to the storage cylinder. By this expansion sufficient cooling

[8] The small diameter German silver tubes used in the construction of the calorimeter had wall thicknesses much greater than would have been necessary simply to withstand the gas pressures to which they were subjected. Experience showed that tubes with walls thinner than those finally used would, in time, develop fissures and fractures due to either or both the mechanical strains which were set up during rapid cooling of the apparatus and the slight corrosive action developed at soldered joints.

[9] K. Mendelssohn, Zeits. f. Physik **73**, 494 (1932).

was produced to cool the dam, and the calorimeter can and its contents, each unit working separately, to 4°K and liquefy sufficient helium in the two chambers so that the temperature of each unit could be still further reduced to below 2°K by boiling off the liquid helium under reduced pressure.

By employing the device of placing a "micro" helium liquefier inside the calorimeter can itself, it was possible to pump the exchange gas out of the vacuum compartment as soon as the cooling with liquid hydrogen had been completed, thus eliminating the necessity for an inner vacuum compartment. It was also of considerable help in securing a high vacuum to get the exchange gas out before the lower temperatures were reached.

When it was time to begin the heat capacity measurements, whatever liquid helium was left in the helium chamber *B* was boiled out by cautiously passing an intermittent current of one milliampere through the constantan thermometer-heater until the temperature showed a slight permanent rise.

An initial helium pressure of 70 atmospheres at 12°K was usually sufficient to produce the desired cooling although pressures up to 140 atmospheres were used when they were available. It was estimated that 1 cc of liquid helium formed in the chamber *B* and 25 cc in the dam *D* when the starting pressure was 75 atmospheres. Extremely pure helium was necessary for the liquefaction operation since even the most minute traces of foreign gases, including hydrogen, proved sufficient to freeze up the small tubes through which the helium chambers were blown down. Especially carefully handled helium supplied in pressure cylinders was further purified by slow passage under high pressure over peat charcoal contained in a series of copper traps immersed in boiling nitrogen. For the satisfactory removal of hydrogen from helium by adsorption on charcoal at liquid air temperatures it was found necessary to pass the gas over the charcoal at high pressures even when the gas was to be used subsequently at low pressures as in the gas thermometer.

Gas thermometer

The fine German silver capillary tube connecting the silver bulb of the standard gas thermometer with the outside of the cryostat was joined, at the top of the cryostat, to a somewhat larger sized tube (0.46 mm i.d.) which led over to the manometer several feet away. The use of a relatively large sized tube in the room temperature part of the connecting system was found to result in much more rapid equalization of pressure in the system without objectionably increasing the dead space correction in the cases of very low temperature measurements. The obnoxious volume in the manometer and connecting tubes amounted to 3 cc.

The manometer for the standard gas thermometer was in most respects similar to that described by Mendelssohn.[9] It consisted of a long and a short limb of 15 mm glass tubing mounted vertically beside each other on a massive stand which could be accurately leveled. A glass manifold for the transmission of mercury connected the lower ends of the two limbs to each other and to a mercury reservoir. The top of the short limb was closed with a brass plug cemented into the end of the glass tube. The German silver tube from the thermometer bulb and another small tube used for purging and filling the bulb were soldered into holes passing through the brass plug. From the center of the underside of the plug protruded a short ivory pointer which served as the fixed reference mark for setting the mercury levels. The top of the long limb was connected to a McLeod gauge and a mercury diffusion pump. Behind the long limb was a mirror-backed, glass scale on which the height of the mercury level could be estimated directly to 0.1 mm. A careful comparison of the levels of the mercury in the two limbs when both were under zero pressure showed that surface displacements due to surface tension were equal in the two limbs.

For the measurements reported in this paper the limbs of the manometer were made from Pyrex glass. It was noted, however, that there was a substantial loss of helium from the thermometer when it was allowed to stand idle for some days with a large surface of Pyrex glass exposed to the gas. Since no ordinary leaks could be detected anywhere in the system, it was concluded that the loss was due to solution of considerable helium in the glass and diffusion through it. The amount of gas lost seemed larger

than would have been expected from the observations of several investigators who have examined this phenomenon.[10, 11] For subsequent measurements a soft glass manometer of the same design was therefore substituted.

Inasmuch as the indications of the gas thermometer were checked against the triple and boiling points of hydrogen at the beginning and end of every series of measurements with satisfactory agreement in every instance we are satisfied that there was no significant loss of helium from either manometer during the seven or eight hours required for a series of measurements. When the manometers were in use the surface of glass exposed to the helium gas was very small.

The standard thermometer was filled with purified helium to a pressure of approximately 1 atmosphere while the bulb was at the normal boiling temperature of nitrogen. This operation was carried out conveniently while the cryostat was being precooled, preparatory to being filled with liquid hydrogen. With this amount of gas in the thermometer the pressure change per degree was roughly 1 cm of mercury at temperatures below 20°K. The constants for the gas thermometer equation were determined twice at the boiling point of hydrogen each time the calorimeter was used. The temperature scale was based on a value of 20.39°K, given by Bonehoffer and Harteck,[12] for the normal boiling point of normal hydrogen. The equation of state data for helium of Onnes, Keesom *et al.*,[13] of F. Henning[14] and of Holborn and Otto[15] were used for converting pressure readings to temperatures on the thermodynamic temperature scale. By means of thermocouples and mercury thermometers, the temperatures of the various thermal zones in the connecting tubes and manometer system were continuously observed and appropriate correction terms introduced into the gas thermometer equation. The volumes of the various parts of the thermometer system were determined by conventional methods.

Electrical measurements

For service both as resistance thermometer and heating element, a coil of No. 40 B. & S. Gauge, double silk covered constantan wire[16] was wound on the outside of the calorimeter can. Prior to the winding of the wire the surface of the can was slightly roughened with fine sandpaper and painted with a moderately thick coat of Bakelite lacquer. The can was then baked at a temperature of 100°C for 10 hours. A heavy coating of lacquer was applied to the surface and also to the wire itself as the wire was wound onto the can. This lacquer was allowed to dry at room temperature for 24 hours and then was baked as before. Despite the different thermal expansions of constantan and silver, the wire remained firmly cemented to the can through repeated coolings and warmings over the period of a year that the calorimeter was in use. Measurements of the temperature head developed between the coil and the material inside the can during heating periods showed that errors introduced into the measurements due to temperature heads could not amount to more than one-tenth of one percent. The thermometer-heater had a resistance of 4800 ohms at 298°K.

Two leads of No. 40 copper wire were joined directly to each end of the constantan coil. For resistance measurements, current was supplied by a thermostated 6-volt storage battery discharging through a 300,000 ohm resistance placed in series with the thermometer. The resistance of the thermometer was measured by comparing the potential drop across the coil itself, by means of the extra set of leads, with the drop across a standardized fixed resistance placed in series with the thermometer. During the determinations of the heat capacity of benzene and of the empty calorimeter all of the potentiometric measurements were made with a White double potentiometer which had recently been checked by the makers. For measurements on the other substances reported in this paper and subsequent papers, a new low range Wenner potentiometer[17] was used for the re-

[10] Baxter and Starkweather, Science **68**, 516 (1928); **73**, 618 (1931).
[11] W. D. Urry, J. Am. Chem. Soc. **54**, 3887 (1932).
[12] Bonehoffer and Harteck, Naturwiss. **17**, 321 (1929).
[13] Leiden Comm. No. 170, Suppl. 51 and 70; Physica **2**, 37 (1935).
[14] F. Henning, Zeits. f. ges. Kälte-Ind. **37**, 169 (1930).
[15] Holborn and Otto, Zeits. f. Physik **30**, 321 (1924); **38**, 365 (1926).

[16] Advance brand.
[17] (a) F. Wenner, Phys. Rev. **31**, 94 (1910); (b) L. Behr, Rev. Sci. Inst. **3**, 109 (1932).

sistance measurements. This instrument had been calibrated by the National Bureau of Standards for an accuracy of 0.01 percent in the ranges of voltages for which the instrument was used.

The electrical instruments were located in a special room where they were protected from sudden changes of temperature. The standard cells used with the potentiometers were frequently compared with a reference cell. All of the cells were enclosed in a cork-lined box which, in turn, was kept in a closed cupboard. The galvanometers were placed thirty feet from the scale on which the deflections were read by the displacement of a focused light beam. Switches constructed entirely of copper and lead sheathed copper wires were used in all the external electrical circuits. The potentiometers, galvanometers, the calorimeter and the connecting wires were all brought under the same shielding system.

The resistance thermometer was frequently compared with the gas thermometer during the progress of every set of heat capacity measurements. Between 2° and 20°K the resistance thermometer exhibited a smooth, continuous relationship between resistance and temperature and between the dR/dT coefficients and temperature. In this range the change in resistance was roughly 0.16 percent per degree. Between 20° and 25°K the resistance became relatively independent of temperature so that the thermometer could not be used above that region. The dR/dT coefficients of the thermometer remained practically constant during the period of a year that the thermometer was in use.

At temperatures above 20°K a single junction pair copper-constantan thermocouple, soldered to the top of the calorimeter can was used to extend the measurements to temperatures where our samples could be compared with those studied by other workers. The ice point was used as the reference junction. The calibration and behavior of this and other thermocouples that were used has been discussed by two of the authors.[18]

The energy used to produce the measured temperature rises was supplied to the constantan thermometer-heater by a large battery of lead storage cells. The heating periods varied from 5 seconds at the very lowest temperatures to 14 minutes at 85°K. For the short heating periods required below 15°K the total energy input was computed by the use of the formula $\Delta H = 0.23904 \times R_{Av} \times I^2 \times t$ where R and I are in international units and t is in units of 1/86400 mean solar day. The mid-time or average resistance of the heater during a heating period was computed from the thermometer readings taken just before and just after the energy input.

For the very short heating periods at temperatures below 4°K the current was determined by measuring the potential drop across a standard resistance placed in series with an accurately adjustable resistance which had been set, as nearly as possible, at the same resistance as the calorimeter heater. As soon as this measurement was completed the current was rapidly switched to the calorimeter. The battery was stabilized by allowing it to flow through the adjustable resistance for some time before the final measurement was made. The change in resistance of the constantan heater was so small and so regular over the short temperature ranges used and the thermal drift of the calorimeter was so small that energy measurements made in this way were well within the limits of the accuracy of the time measurements.

During the heating periods of several minutes duration, used between 4° and 15°K, the current was measured directly while it was flowing through the heater. During the longer heating periods, permissible above 15°K, the potential across the heater was also measured directly at the half-time by means of a volt box circuit and the total energy input calculated in the conventional manner.

The timing of the heating periods was done with two calibrated stopwatches, operated manually. The absolute error in the timing did not exceed 0.3 second.

Accuracy and remarks

The heat capacity of the empty calorimeter was determined by measurements carried out in exactly the same way as those on the substances studied. Below 20°K the heat capacity of the empty calorimeter can, including the enclosed helium liquefier and the gas thermometer bulb,

[18] Ahlberg and Lundberg, J. Am. Chem. Soc. **57**, 2722 (1935).

was about 45 percent of the 0.60 mole sample of benzene that was studied.

Below 4°K the over-all accuracy of the data obtained was determined both by the time and the temperature difference measurements. Above 4°K the temperature difference measurements were the primary factor in determining the over-all accuracy. With the possible exception of the measurements below 5°K, the reported heat capacity values are estimated to be within 2 percent of the true values at all temperatures. On the basis of mutual consistancy within the series, the measurements obtained in most of the runs were well within a 2 percent limit. At the very lowest temperatures at which measurements were obtained the heat capacity of the helium gas, which was placed in the calorimeter can to promote heat conduction, began to be an appreciable part of the total measured heat capacity and introduced an additional element of uncertainty.

When the calorimeter was designed it was intended that the thermocouples would be used only for control and comparison purposes at relatively high temperatures. But the excellent degree of thermal isolation which the calorimeter can displayed when the calorimeter was in operation led us to make complete sets of measurements up to 95°K in several cases with all of the care which the accuracy and sensitivity of the thermocouples justified.

Two to three liters of liquid hydrogen were required for a cooling of the calorimeter. In filling the cryostat the liquid hydrogen was piped through small, articulated glass "Dewar tubes" directly from the main laboratory liquefier which stood some distance from the calorimeter. The use of intermediate transfer vessels was thus eliminated to considerable advantage. About 45 liters of liquid nitrogen were required for a complete experiment which included the precooling of the calorimeter, the liquefaction of hydrogen, the purification of helium and keeping filled for twenty-four hours the nitrogen well in which the cryostat was immersed.

Materials

Benzene

The benzene sample was taken from a batch of Baker's "C. P. Analyzed" material. The freezing point of the material was determined by a time temperature experiment and found to be 4.92°C, indicating a probable purity of 99.1 mole percent. A higher degree of purity would have been of no virtue for measurements in the temperature range studied.

Methyl alcohol

This substance was supplied to us by Dr. J. C. Woodhouse of E. I. du Pont de Nemours and Company and was described as of excellent purity. The density of the material, as determined by us, was $d_4^{25}=0.78631$. If it is assumed that water was the only impurity, the material was 99.7 mole percent methyl alcohol.

In the work with benzene and methyl alcohol, care was taken to cool the calorimeter slowly through the freezing region of the substances in order to insure complete crystallization. While the cryostat was at room temperature helium gas was admitted to the vacuum compartment to a pressure of about 1 cm. Liquid nitrogen was then transferred intermittently in small portions into the hydrogen Dewar vessel which surrounded the vacuum compartment until the whole apparatus had cooled to 78°K. The nitrogen was removed from the cryostat just before the liquid hydrogen was run in. Visual observations made by plunging test tubes of benzene and methyl alcohol directly into liquid air indicated that, even with such drastic cooling rates, crystallization would proceed to completion. The observations of Kelley[19] indicate that the high temperature modification of crystalline methyl alcohol does not tend to supercool.

Glycerol

Three studies were made on a single sample of this substance. A batch of Baker's "C. P." glycerol was distilled through an all glass still under a pressure of less than 1 cm of mercury at a temperature of 170°C. The sample for the heat capacity measurements was taken from the middle one of three equal fractions that were collected. The purity of the material was attested to by the fact that very little evidence of premelting was apparent when the sample was fused after crystallization. Two sets of measurements were made with the material in the glassy

[19] K. K. Kelley, J. Am. Chem. Soc. **51**, 180 (1929).

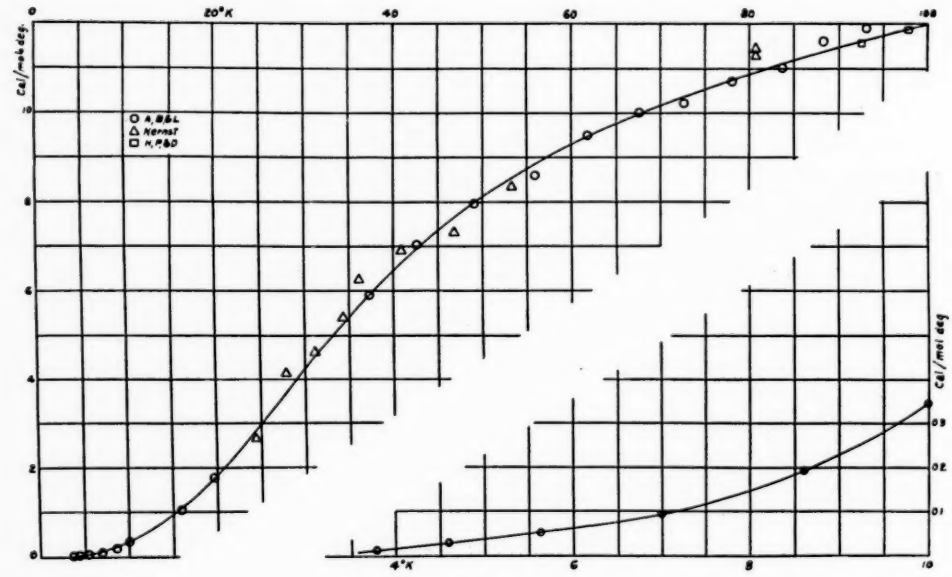

FIG. 2.

state and one with it crystallized. The chronological order of the measurements was: glass I, crystals, glass II.

Glass I was formed from material which had never been in the crystalline state, at least since it had been distilled. In order to effect rapid cooling of the sample in the calorimeter, the vacuum compartment was pumped out and the calorimeter can warmed to 300°K while the cryostat was being filled with liquid nitrogen. When the walls of the vacuum compartment had cooled the vacuum was broken by the admission of an exchange gas.

Following the measurements on glass I, the sample was crystallized, without seeding, by allowing it to warm up extremely slowly from about 200°K.[20] Crystallization set in at approximately 257°K. The material was remelted and recrystallized several times, always without difficulty, to insure the dependability of the procedure. Before cooling the material for the heat capacity measurements, the crystallized glycerol was held, in the calorimeter, at 283°K for several days to insure complete crystallization and then cooled slowly with liquid air.

Glass II was formed following the melting of the crystals, without, moreover, ever permitting the temperature of the glycerol to rise above 300°K. To insure complete fusion, the material was held, in the calorimeter, at 298°K for several days before the formation of the glass. In the formation of this glass the calorimeter was cooled relatively slowly by the technique used in the cases of benzene and methyl alcohol.

[20] Gibson and Giauque, J. Am. Chem. Soc. **45**, 93 (1923).

BENZENE AND METHYL ALCOHOL

The experimental values of the molal heat capacities of benzene at constant pressure are shown in Table I and Fig. 2. The electrical

TABLE I. *Molal heat capacities of benzene. Molecular weight 78.05: moles in sample 0.6004. 0°C=273.17°K: 1 calorie=4.185 abs. joules.*

T °K	ΔT	C_p cal./deg./mole	C_p/T^3
3.79	0.32	0.0125	2.30×10^{-4}
4.60	.48	0.0302	3.10×10^{-4}
5.63	1.14	0.0525	2.94×10^{-4}
7.00	1.40	0.095	2.77×10^{-4}
8.60	1.64	0.192	3.02×10^{-4}
10.02	1.64	0.347	3.45×10^{-4}
15.90	2.28	1.07	2.66×10^{-4}
19.82	2.42	1.80	2.31×10^{-4}
37.35	5.13	5.90	
42.82	5.75	7.03	
49.01	6.36	7.96	
55.97	6.27	8.60	
61.88	5.64	9.5	
67.56	5.31	10.0	
72.71	5.10	10.2	
78.08	5.80	10.7	
83.59	5.60	11.0	
88.21	5.36	11.6	
93.16	5.23	11.9	

energy used for heating was measured in International units and converted to calories by the use of the definition: 1 calorie = 4.1833 Int. joules. Before computing the number of mole in the samples the weights of the materials were reduced to "in vacuum" values. Below 20°K the temperature measurements were made by a joint employment of the helium gas thermometer and the constantan resistance thermometer. Above 20°K the temperatures were measured with the copper-constantan thermocouple. In the case of benzene the measurements made with the thermocouple unfortunately did not prove as consistent and satisfactory as some of those made subsequently on other substances.

In Table II are given the molal heat capacities as read off the most plausible curve through the observations (the solid curves of Fig. 2). In constructing the curve at points where there was any element of choice, due weight was given to the measurements of Nernst[21] between 20° and 80°K and those of Huffman, Parks and Daniels[22] starting at 92°K. Applications of the new heat capacity data for benzene have been made by Lord and Andrews[23] and by Lord, Andrews and Ahlberg[24] in papers published elsewhere.

The entropy of benzene at various temperatures is shown in Table III. The usual graphical method of integration was employed for our own heat capacity data. The value of the entropy at 3°K was approximated by the use of the conventional rule $S_T = aT^3/3$ in which the value of "a" was determined from the heat capacity measurements below 9°K and found to have the value 2.85×10^{-4} cal./deg.^{4}/mole. The new experimental value of the entropy at 90°K is 0.46 E. U. lower than the value based on extrapolation given by Huffman, Parks and Daniels.[22] The entropy data of the latter authors were employed in computing the entropies given for temperatures above 90°K.

Experimental values of the molal heat capacities of methyl alcohol from 3° to 28°K are given in Table IV. The measurements were made in a manner exactly similar to those on benzene. The agreement of our values with those of Kelley[19] in the interval between 16° and 30°K is satisfactory. Several of Kelley's measurements are included, in italics, in Table IV for comparison. In Table V the entropy at various temperatures has been computed. The T^3 formula was used rather arbitrarily to estimate the value of the entropy at 3.25°K. As will be noted in the last column of Table IV, the C_p/T^3 quotient is not constant below 7°K but diminishes in a rather regular manner with the temperature. A very similar but somewhat more pronounced effect was also obtained in the measurements on crystalline glycerol. The drift is larger than our estimate of the random errors in the measurements but may be due to a systematic error. Between 7° and 15°K the obedience to the T^3 law is quite satisfactory. For a practical estimation of the numerical value of the entropy at 3.25°K almost any simple function of the temperature can be made to serve almost equally well for the extrapolation of the heat capacity data.

Kelley gives a value of 0.26 E.U. for the entropy at 16.5°K, based on extrapolation, which is in agreement with our value of 0.267 E.U. based on experimental measurements

TABLE II. *Molal heat capacities of benzene. Read from smooth curve through observations. Molecular weight 78.05. 0°C = 273.17°K: 1 calorie = 4.185 abs. joules.*

T °K	C_p cal./deg./mole	T °K	C_p cal./deg./mole
4	0.0195	40	6.47
6	.065	50	8.14
8	.147	60	9.32
10	.346	70	10.16
15	.920	80	10.85
20	1.84	90	11.44
25	3.00	100	11.99
30	4.24		

TABLE III. *Entropy of benzene.*

T °K	S cal./deg./mole
0	0
3.63	0.0045(a)
10.0	0.098
20.0	0.73
90.0	10.89
278.6 Crystals	30.91(b)
278.6 Liquid	39.34
298.1	41.49

(a) By extrapolation $S = aT^3/3$ where $a = 2.85 \times 10^{-4}$.
(b) Values above 90°K based on the data of Huffman, Parks and Daniels, J. Am. Chem. Soc. **52**, 1554 (1930).

[21] W. Nernst, Ann. d. Physik **36**, 395 (1911).
[22] Huffman, Parks and Daniels, J. Am. Chem. Soc. **52**, 1547 (1930).
[23] Lord and Andrews, J. Phys. Chem. **41**, 149 (1937).
[24] Lord, Andrews and Ahlberg, to be published.

TABLE IV. *Molal heat capacities of methyl alcohol. Molecular weight 32.03: moles in sample 1.426. 0°C=273.17°K: 1 calorie=4.185 abs. joules.*

T °K	ΔT	C_p cal./deg./mole	C_p/T^3
3.68	0.86	0.0067	1.35×10^{-4}
4.65	.90	.0139	1.38
5.44	.80	.0252	1.56
6.30	.98	.0427	1.70
7.33	1.19	.071	1.80
8.58	1.29	.110	1.75
9.73	1.24	.165	1.79
10.75	1.37	.235	1.89
12.28	1.82	.359	1.93
14.37	2.48	.517	1.75
16.94	3.13	.817	1.68
18.80		*1.11*(a)	
20.50	4.76	1.29	
21.55		*1.51*(a)	
23.94	2.92	1.94	
24.43		*1.96*(a)	
27.25		*2.29*(a)	
28.39	3.77	2.57	

(a) Measurements by K. K. Kelley, J. Am. Chem. Soc. **51**, 180 (1929).

down to 3.25°K. Data by Kelley were employed in computing the value given for the entropy at 298.1°K.

GLYCEROL

It has been suggested[25] that glasses of the same substance formed under different conditions should display slight differences in their fundamental properties at low temperatures. For some substances, at least, it seems necessary to conclude that the liquid state is not one of complete randomness but rather that there is some slight degree of order or orientation among the particles which varies inversely as the temperature. In a viscous liquid, moreover, there must be an appreciable lag in the attainment of the degree of order corresponding to the new temperature state when the temperature is decreased rapidly through a considerable interval. Furthermore, the changes which occur when a liquid such as glycerol passes through its "congealing zone" may reasonably be assumed to involve an inhibition or extreme slowing up of the processes by which an equilibrium state of order is arrived at. These considerations made it seem not altogether inconceivable that glasses which had been cooled through their congealing zone at rapid but different rates might show significant differences in their heat capacities at very low temperatures where the heat capacity is determined wholly by the structural configuration and properties of the solid state. With these ideas in mind, the sample of glycerol was congealed twice, as described above, under circumstances as different as it was possible to make them. The measurements on the glass designated as glass I were extended from 2.3° to 85°K while those on the glass designated as glass II were only carried up to 22°K. Starting at 14°K the observed heat capacity values for glass II fall slightly below those of glass I by increasing amounts up to 22°K where the measurements on glass II were unfortunately interrupted. The best curves drawn through the two sets of measurements indicate a difference in heat capacity between the two glasses of some 0.13 calorie per mole at 18.5°K. Below 14°K the heat capacities of the two glasses differ irregularly and by amounts substantially less than the limits set by experimental uncertainty. The present data are not adequate for a decision as to the reality of this apparent difference which presumably ought to be more pronounced rather than less at the lower temperatures. It may be said, however, that the two glasses are certainly quite similar if not altogether identical in structure.

The molal heat capacities of glassy and crystalline glycerol at constant pressure are shown in Tables VI and VII, respectively, and in Figs. 3 and 4. Since it does not seem justifiable to weight the small differences observed above 14°K in the heat capacities of the two glasses, the data on both are included in Table VI. The results of the very brief series of measurements between 10° and 12°K by Simon and Lange[26] are included, in italics, in Tables VI and VII. The agreement with the present measurements is good, particularly so in the case of the crystalline

TABLE V. *Entropy of methyl alcohol.*

T °K	S cal./deg./mole
0	0
3.26	0.00154(a)
16.25	0.267
298.1	30.3(b)

(a) By extrapolation.
(b) Based on the data of Kelley (reference 19) above 20°K.

[25] F. Simon, Zeits. f. anorg. allgem. Chemie **203**, 219 (1931).

[26] Simon and Lange, Zeits. f. Physik **38**, 227 (1926).

TABLE VI. *Molal heat capacities of glassy glycerol. Molecular weight 92.06: moles in sample 0.8049. 0°C=273.17°K: 1 calorie=4.185 abs. joules.*

Glass	T °K	ΔT	C_p cal./deg./mole	C_p/T^3
I	2.30	0.20	0.0037	3.04×10^{-4}
I	2.63	0.12	0.0081	4.45
I	3.03	0.21	0.0055	1.98
II	3.33	0.33	0.0122	3.30
I	3.43	0.19	0.0091	2.25
I	3.66	0.28	0.0131	2.67
II	4.01	0.67	0.0177	2.75
I	4.22	0.57	0.0211	2.81
II	4.75	0.75	0.0339	3.16
I	5.45	0.49	0.052	3.21
II	5.57	0.91	0.057	3.32
I	6.28	1.24	0.085	3.43
II	6.56	1.05	0.104	3.68
I	7.37	1.10	0.148	3.70
II	7.68	1.31	0.163	3.60
I	8.40	1.07	0.230	3.88
II	9.12	1.71	0.282	3.72
I	10.52	0.99	0.435	3.74
(a)	*10.58*		*0.413*	*3.50*
(b)	*10.84*		*0.433*	*3.37*
II	10.88	1.85	0.461	3.58
(a)	*11.67*		*0.524*	*3.32*
(b)	*12.26*		*0.578*	*3.14*
I	12.33	2.65	0.614	3.28
(a)	*12.69*		*0.636*	*3.11*
II	13.10	2.62	0.722	3.21
I	14.80	2.33	1.02	3.15
II	15.90	2.90	1.10	2.74
I	17.16	2.37	1.35	2.67
II	18.81	2.91	1.52	2.28
I	19.75	2.79	1.80	2.33
I	22.62	2.92	2.34	
I	28.98	3.28	3.45	
I	32.05	2.85	3.86	
I	34.88	2.82	4.43	
I	37.45	2.44	5.00	
I	40.33	3.13	5.36	
I	44.14	4.74	6.03	
I	51.19	5.69	7.05	
I	57.37	6.65	8.02	
I	63.65	5.94	8.99	
I	69.37	5.51	9.65	
I	74.37	5.22	10.17	
I	79.68	5.60	11.23	
I	85.12	5.28	12.00	
I	90.12	5.14	12.29	
I	94.89	4.87	13.12	

(a) Measurement of Simon and Lange, Series I.
(b) Id.; Series II, Zeits. f. Physik **38**, 227 (1926).

TABLE VII. *Molal heat capacities of crystalline glycerol. Molecular weight 92.06: moles in sample 0.8049. 0°C=273.17°K: 1 calorie=4.185 abs. joules.*

T °K	ΔT	C_p cal./deg./mole	C_p/T^3
3.08	0.59	0.0051	1.74×10^{-4}
3.86	0.77	0.0093	1.62
5.03	1.57	0.0193	1.52
6.30	1.31	0.0414	1.66
7.44	1.27	0.070	1.70
8.51	1.19	0.116	1.88
9.66	1.33	0.172	1.91
10.57		*0.242*(a)	*2.06*
10.67		*0.239*(b)	*1.97*
10.98	1.62	0.266	2.01
11.96		*0.353*(a)	*2.07*
12.47	1.83	0.413	2.13
12.83		*0.438*(b)	*2.07*
12.91		*0.438*(a)	*2.04*
14.58	2.39	0.629	2.03
17.45	3.03	0.983	1.85
19.54	1.22	1.282	1.72
21.89	3.42	1.621	1.54
25.25	3.65	2.19	
29.55	5.03	2.88	
35.36	6.17	3.82	
42.96	8.00	5.17	
49.19	4.14	6.32	
54.57	6.02	7.22	
61.00	5.15	8.13	
66.81	5.53	9.12	
72.34	5.12	9.86	
77.45	4.78	10.62	
82.33	4.53	11.21	
86.92	4.31	11.90	

(a) Measurements of Simon and Lange, Series I.
(b) Id., Series II; Zeits. f. Physik **38**, 227 (1926).

form. Above 80°K our measurements tie in well with those of Gibson and Giauque.[27]

In Table VIII, column I is a tabulation of the entropies of the crystalline state at various temperatures, assuming that the crystalline form obeys the so-called third law of thermodynamics. The value of 9.05 E.U. for the entropy at 90°K is 0.8 E.U. lower than the value given by Parks, Kelley and Huffman[28] who extrapolated the data of Gibson and Giauque[27] and of Simon and Lange.[26] The data of Gibson and Giauque were employed in computing the values given for temperatures above 90°K. Column II of Table VIII gives values of the integral $\int_0^T C_p d \ln T$ for the glassy form.

If it is assumed, in the absence of conclusive evidence to the contrary, that the liquid ordinarily resulting from the melting of a glycerol crystal and the liquid resulting from the softening of a glycerol glass are thermodynamically identical and therefore possess identical entropy, the following equality will, by thermodynamics, hold for the liquids at the melting point of the crystal.

$$S_{(l)}^{291} = \int_0^{291} [C_{p(\text{cry.})} d \ln T] + \Delta S_f + S^0_{(\text{cry.})}$$
$$= \int_0^{291} [C_{p(\text{gl.})} d \ln T] + S^0_{(\text{gl.})},$$

[27] Gibson and Giauque, J. Am. Chem. Soc. **45**, 93 (1923).

[28] Parks, Kelley and Huffman, J. Am. Chem. Soc. **51**, 1969 (1929).

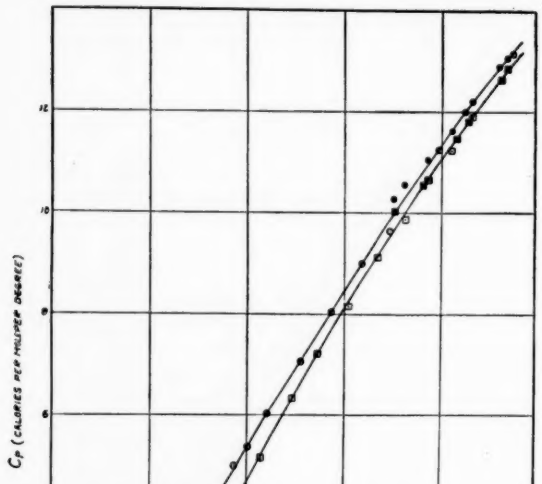

FIG. 3.

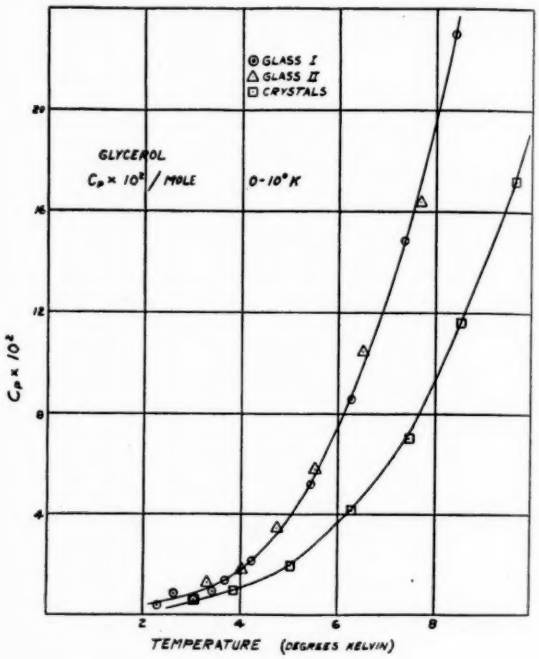

FIG. 4.

where ΔS_f is the entropy change involved in the melting of the crystal form at 291°K; $S^0_{(cry.)}$ has the value zero according to the third law, and $S^0_{(gl.)}$ is the apparent entropy of the glassy form at 0°K. The entropy difference between the two forms at any temperature below the melting point is therefore given by

$$\Delta S_{(gl.-cry.)} = \Delta S_f - \int_T^{T_{MP}} [C_{p(gl.)} - C_{p(cry.)}] d \ln T, \quad \text{(I)}$$

while $S^0_{(gl.)}$ is obviously obtained by setting the lower limit of the integral at zero. The values of the entropy differences between the two forms at various temperatures as given by this equation are shown in column III of Table VIII. The accuracy with which $S^0_{gl.}$ can now be given is limited by the experimental accuracy of the heat of fusion and the high temperture heat capacities. An appraisal of the existing high temperature data indicates that the value of $S^0_{gl.}$ is 4.64±0.04 E.U. In order to take advantage of the accuracy of our low temperature measurements for showing the temperature trend of the entropy differences between the crystalline and glassy forms of the substance, the values of

$$\int_0^T [C_p d \ln T]_{(gl.)} - S_{T(cry.)}$$

are given in column IV.

The importance of heat capacity data at very low temperatures for a correct picture of the solid state of "soft" substances is illustrated by Figs. 3 and 4. At liquid-air temperatures the heat capacity curves of crystalline and glassy glycerol are very close together and appear to run practically parallel to each other. Proceeding downward, the curves begin to diverge in no uncertain manner at about 50°K as differences in heat capacity due to differences between the structure of the crystalline and glassy states begin to have measurable effect on the total observed heat capacities. In Fig. 4 the curves appear to be converging rapidly but this is an effect due to the rapidly diminishing absolute values of the two sets of heat capacities. At 18°K the heat capacity of the glass is larger than that of the crystal by 40 percent of the latter, at 12° by 55 percent and

between 9° and 5° by 100 percent. As column IV of Table VIII shows, this divergence of the heat capacity curves is sufficient to produce an error of +1 E.U. if an attempt is made to evaluate $S^0_{gl.}$ by extrapolating the high temperature heat capacity data.

The present measurements confirm the conclusions and predictions of Simon and Lange[26] about the behavior and significance of the low temperature heat capacities of crystalline and glassy glycerol and little need be added here to their discussion. They predicted an entropy for the glass at the absolute zero of 4.6±0.3 E.U. which is in agreement with our value of 4.64±.04 E.U. Unless decidedly *ad hoc* assumptions as to the behavior of the heat capacity below 3°K are to be admitted, it seems safe to conclude that the four glasses which have been studied at very low temperatures (two by Simon and Lange and two in this investigation) retain 4.6 units of entropy at the absolute zero. This, however, is undoubtedly the residual entropy of a frozen-in state which is an equilibrium state of the glass only at or above the congealing temperature (180°K) rather than the entropy of an "ideal glass" at the absolute zero. Amorphous states formed by a cooling path radically different from those which can be obtained in the types of vacuum calorimeters that have been employed might well show a measurably different entropy at the absolute zero.

TABLE VIII. *Entropies of crystalline and glassy glycerol. I. Entropies of crystalline glycerol at the indicated temperatures and, above 291°K, of liquid glycerol. II. Values of the integral* $\int_0^T C_p d \ln T$ *for the glassy state and super-cooled liquid. III. Entropy differences between the glassy and crystalline forms,* $S_{gl.} - S_{cry.}$ *as computed by Eq. (I). IV. Values of* $\int_0^T (C_p d \ln T)_{gl.} - S_{T(cry.)}$.

T °K	I cal./deg./mole	II cal./deg./mole	III cal./deg./mole	IV cal./deg./mole
0.0	0.0	—	4.64(a)	—
2.20	0.00058(b)	0.00088(b)	4.64	0.0003
2.79	0.0012(b)	0.0018	4.64	0.0006
10.00	0.0472	0.119	4.71	0.072
20.00	0.505	0.784	4.92	0.279
70.00	6.307	7.290	5.62	0.983
90.00	9.052	10.118	5.71	1.066
291.00	32.58(c)	42.96(c)	15.02(c)	
Liquefaction, $-S_{fusion} = 15.02$(c)				
291.00	47.60			
298.10	48.87			

(a) ±0.04 E.U.
(b) By extrapolation.
(c) Computed using the data of Gibson and Giauque for temperatures above 90°K. (J. Am. Chem. Soc. **45**, 93 (1923); see also Parks, Kelley and Huffman, J. Am. Chem. Soc. **51**, 1971 (1929).)

The authors are indebted to the United States Navy Department and especially to Mr. C. E. Earle for the trouble taken in supplying pure helium gas for use in the liquefier. To Professor D. H. Andrews the authors are most grateful for his part in putting the equipment of the Cryogenic Laboratory at their disposal and to Messrs. W. T. Ziegler and C. F. Squire for assistance in the calculations and graphical work.

Electronic Activation in Crystals: The Heat Capacities of $Sm_2(SO_4)_3 \cdot 8H_2O$ and $Nd_2(SO_4)_3 \cdot 8H_2O$ from 3 to 40° Kelvin

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The heat capacities of the sulfate octahydrates of neodymium and samarium have been measured from 3 to 40°K. The results have been applied to the study of the electronic energy states of the rare earth ions. The electronic heat capacity of the neodymium ion in the sulfate octahydrate has been determined. The separations of the two electronic energy levels comprising the basic states of both salts have been found to be less than 1 cm^{-1}. The presence of an electronic energy level in $Nd_2(SO_4)_3 \cdot 8H_2O$ at 77 cm^{-1} above that of the basic state has been substantiated. The statistical weight of this level appears to be twice that of the basic state.

THE electronic energy levels of the metal ion in a crystalline salt of a rare earth metal can be investigated by several rather independent experimental approaches. Studies of their spectra, their magnetic susceptibilities and their heat capacities all may be used as sensitive tools for making apparent the existence and characteristics of the energy levels of the rare earth metal ions. The use of heat capacity measurements in the study of electronic activation in crystals has been developed by Ahlberg and Freed[4] for the case of the (Sm^{+++}) ion in samarium sulfate octahydrate. For reasons brought out most conveniently in the discussion which is given below, the data for the study of the samarium ion in crystals have been extended by the determination of the heat capacity of its salt down to 2°K. To supplement the existing experimental and theoretical work on the magnetic and optical properties of the (Nd^{+++}) ion the heat capacity of neodymium sulfate octahydrate has been measured between 3° and 40°K.

Experimental

The heat capacities of the salts were determined in the calorimeter which has been described in detail by Ahlberg, Blanchard and Lundberg.[5] The measurements reported here were made immediately following those described in the paper mentioned and by the same methods.

Materials

The sample of neodymium sulfate octahydrate, $Nd_2(SO_4)_3 \cdot 8H_2O$, used in the calorimeter weighed 50.03 grams (0.1388 mole). The salt was prepared from a sample of neodymium ammonium nitrate hydrate purchased from the Welsbach Company, Gloucester, New Jersey. Concerning the rare earth metal impurities in this sample Dr. H. S. Miner, chief chemist, Welsbach Company, wrote, "the neodymium ammonium nitrate is of a high grade and conforms to the theoretical composition. It is supposed to be free from lanthanum and praseodymium although there may be a slight trace of the latter." The neodymium salt, as received, was first converted to the oxide. Slightly less than the stoichiometric equivalent of sulfuric acid in 50 percent solution was added to the oxide slowly. The resulting sulfate was three times dissolved and recrystallized. The latter operation was carried out by evaporating at 85–90°C most of the water in excess of that required by the formula of the octahydrate. The saturated solutions remaining each time were drained from the crystals. After the last crystallization the crystals were washed several times with cold water and then dried at room temperature by exposure to air of normal humidity. Analysis of the neodymium sulfate octahydrate gave a water content of 20.01 percent (theoretical—20.03 percent).

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[4] Ahlberg and Freed, Phys. Rev. **39**, 540 (1932); J. Am. Chem. Soc. **57**, 431 (1935).
[5] Ahlberg, Blanchard and Lundberg, J. Chem. Phys. **5**, 539 (1937).

The sample of samarium sulfate octahydrate, $Sm_2(SO_4)_3 \cdot 8H_2O$, employed for the measurements weighed 51.01 grams (0.13915 mole). This salt was loaned to us by Professor H. N. McCoy to whom we are much indebted. Professor McCoy stated that the sample was of a very high degree of purity. We recrystallized the salt once again from water by a procedure similar to that used in the case of the neodymium salt. Analysis of the samarium sulfate octahydrate gave a water content of 19.70 percent (theoretical—19.66 percent).

Experimental accuracy

While it is difficult to determine closely the absolute accuracy of the measurements, it is estimated that values read from a smooth curve drawn through the experimental data are everywhere within two percent of the true heat capacities of the salts except as noted below. Inspection of Table II will show that the value given at 24.61°K for $Nd_2(SO_4)_3 \cdot 8H_2O$ is not consistent with respect to the trend of the values at adjacent temperatures. Presumably such an anomaly could arise only from either a phase transition or an experimental error. The former possibility is improbable, however, and consequently little weight should be accorded to the value reported for 24.61°K. The experimental values at 2.62° and 3.00°K for $Sm_2(SO_4)_3 \cdot 8H_2O$ and $Nd_2(SO_4)_3 \cdot 8H_2O$, respectively, suggest an increase in heat capacity at lower temperatures. In connection with these values it should be borne in mind, however, that the heat capacities of the salts at such low temperatures are smaller than that of the gas placed in the calorimeter can to promote rapid heat conduction. Consequently, the values at the lowest temperatures should be considered as only indicative of the order of magnitude of the heat capacity. On the other hand, attention is called to the fact that the quantities of the two salts used in the calorimeter were very nearly equal on a mol basis and further that the apparatus, temperature scales and manipulations in the two sets of measurements were identical. For these reasons many possible sources of systematic error are of little consequence when the measurements are employed for comparative purposes.

Discussion and Conclusions

Samarium ion

Magnetic and spectroscopic measurements have shown that between 10° and 300°K the electrons in $Gd_2(SO_4)_3 \cdot 8H_2O$ undergo practically no thermal excitation. It has also been shown[4] that the elastic vibrations of the crystals in rare earth salts of the same type formula and same crystalline structure as $Gd_2(SO_4)_3 \cdot 8H_2O$ have very nearly the same heat capacities as those of the latter salt crystal. Any distinct excess of heat capacity over that of $Gd_2(SO_4)_3 \cdot 8H_2O$ displayed by a salt of the type mentioned may therefore be attributed to the appropriation of thermal energy by the process of redistribution of the electrons in the various possible energy states with each new increment of temperature.

The heat capacity of $Gd_2(SO_4)_3 \cdot 8H_2O$ has been determined in two separate investigations.[6, 7] The results of these two sets of measurements are in excellent agreement in the ranges of temperatures which apply to the present problem. The heat capacity of $Sm_2(SO_4)_3 \cdot 8H_2O$ has been measured from 17° to 300°K by Ahlberg and Freed.[4] At 17° the heat capacity of $Sm_2(SO_4)_3 \cdot 8H_2O$ exceeds that of $Gd_2(SO_4)_3 \cdot 8H_2O$ by a few hundredths of a calorie per degree per $\frac{1}{2}$ mole of salt. But with mounting temperature the differences between the heat capacities of the two salts increase regularly to a maximum of 1.9 calories at 100°K and then diminish gradually in the temperature interval between 100° and 250°K. These "anomalous" increments of heat capacity in $Sm_2(SO_4)_3 \cdot 8H_2O$ have been identified with a redistribution, with changing temperature, of the electrons into the four states which are found spectroscopically and which are assumed to be doubly degenerate. Theoretically one would expect only three doubly degenerate levels since the ground state of the samarium ion is ${}^6H_{5/2}$. The experimental fact that there are four states and the possible reasons for their occurrence have been discussed by Van Vleck.[8]

The most general equation relating heat capac-

[6] Giauque and Clark, J. Am. Chem. Soc. **54**, 3135 (1932).
[7] Ahlberg and Clark, J. Am. Chem. Soc. **57**, 437 (1935).
[8] Van Vleck, J. Phys. Chem. **41**, 57 (1937).

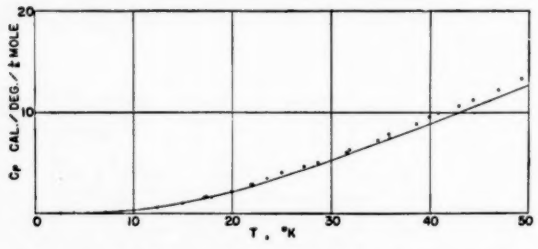

FIG. 1. $Sm_2(SO_4)_3 \cdot 8H_2O$. Dots indicate measured heat capacities (this research); circles, measured heat capacities (Ahlberg and Freed); straight line, heat capacity of lattice vibrations.

ity to the energy levels in a substance is given by

$$\frac{dE}{dT} = \frac{N^2}{RT^2}\left[\frac{\Sigma \epsilon^2 p e^{-\epsilon/RT}}{\Sigma p e^{-\epsilon/RT}} - \left(\frac{\Sigma \epsilon p e^{-\epsilon/RT}}{\Sigma p e^{-\epsilon/RT}}\right)^2\right], \quad \text{(I)}$$

where p represents the statistical weights and ϵ the energies of the respective states.[9] The values for the electronic energy states of $Sm_2(SO_4)_3 \cdot 8H_2O$ employed by Ahlberg and Freed[4] in their calculations were 0, 160, 188 and 225 cm^{-1} as indicated by the adsorption spectra studies of Spedding and Bear.[10] The existence of these energy levels when the (Sm^{+++}) ion lies in a salt crystal is presumably due to the splitting of the normal electronic energy states of the ion by the electric field set up by the ionic lattice structure of the crystal. But when such separations of a multiplet of an odd electronic state occur, the electric field in the crystal is unable to completely remove the degeneracy of the state. Each of the levels is at least doubly degenerate. Since, however, the magnetic interaction of the (Sm^{+++}) ions can remove this degeneracy, there seemed to be a fair possibility that the energy differences of the two lowest states might be such that the heat capacity increment associated with a change in distribution of electrons between the two lowest states would be measurable at temperatures below 15°K. To investigate this possibility the heat capacity of $Sm_2(SO_4)_3 \cdot 8H_2O$ was measured down to 2.6°K. The results are presented in Table I and Figs. 1 and 3. The heat capacity curve for the salt below 15°K proves to be of the type which adequately is accounted for by the usual picture of elastic vibrations in the crystal lattice. That is to say, it conforms as well as reasonably may be expected to the T^3 approximation for lattice specific heats at very low temperatures.[11]

Eq. (I) can be used for the calculation of the maximum separation of the two energy states provided the heat capacity is known. Such a calculation with our data leads to the conclusion that the separation of the two lowest electronic states of the (Sm^{+++}) ion in $Sm_2(SO_4)_3 \cdot 8H_2O$ due to magnetic interaction of the ions is less than one (1) cm^{-1}.

Neodymium ion

Gorter and de Haas[12] have measured the magnetic susceptibility of $Nd_2(SO_4)_3 \cdot 8H_2O$ from 14° to 288°K and have plotted the reciprocals of the magnetic susceptibilities against the temperatures. The observed deviation of their curve from a straight line below 75°K was regarded as evidence that the electrons undergo a redistribution among several possible energy states. Penney and Schlapp[13] have calculated, by theory, the effect of the electric field set up by the ions surrounding the (Nd^{+++}) ions on the magnetic susceptibility and obtained qualitative agreement with the experiments. To continue the study of the problems raised by this work it seemed worthwhile to measure the heat capacity of $Nd_2(SO_4)_3 \cdot 8H_2O$ from 3° to 40°K. The results of the measurements are recorded in Table II and Figs. 2 and 3. An inspection of the curve of Fig. 2 makes it quite

TABLE I. *Heat capacity of 366.59 g (½ mole) $Sm_2(SO_4)_3 \cdot 8H_2O$.*

T_{Av} °K	ΔT	C_p per ½ mole in cal./deg.
2.62	0.63	0.017
3.94	1.39	.023
5.38	1.60	.047
7.10	2.42	.109
8.64	2.59	.187
12.39	2.01	.596
14.94	2.48	1.01
17.88	3.59	1.60
19.91	3.60	2.15
23.50	3.53	3.47
27.25	4.23	4.70
31.44	4.48	6.06
35.83	5.41	7.55
40.80	5.07	9.90

[9] Giauque, J. Am. Chem. Soc. **52**, 4214 (1930).
[10] Spedding and Bear, Phys. Rev. **46**, 975 (1934).
[11] $C_p = 0.000300 T^3$ cal./deg./½ mole of salt (see Fig. 2).
[12] Gorter and de Haas, Leiden Comm. No. 218B, p. 17; Proc. Kon. Akad. Amst. **34**, 1243 (1931).
[13] Penney and Schlapp, Phys. Rev. **41–2**, 194 (1932).

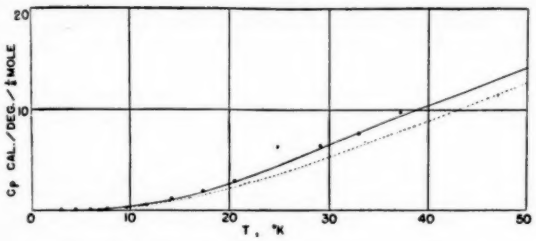

FIG. 2. $Nd_2(SO_4)_3 \cdot 8H_2O$. Dots, measured heat capacities; straight line, constructed from theoretical spectroscopic values; dotted line, heat capacity of lattice vibrations.

apparent that there is a measurable fraction of the specific heat of $Nd_2(SO_4)_3 \cdot 8H_2O$ which must be assigned to the thermal excitation of the electrons. Simon and Kurti[14] have shown experimentally that the heat capacity of $Gd_2(SO_4)_3 \cdot 8H_2O$ cannot be employed to chart the "elastic vibration" heat capacity of other rare earth salts below 10°K. However, a combination of the heat capacity of $Sm_2(SO_4)_3 \cdot 8H_2O$ up to 15°K, as given by this research, with that of $Gd_2(SO_4)_3 \cdot 8H_2O$ at higher temperatures gives the heat capacities of the crystal lattice of this type of salt with sufficient accuracy. The difference between the estimated lattice heat capacities and the observed heat capacities gives the electronic heat capacities directly. The experimental electronic heat capacities of $Nd_2(SO_4)_3 \cdot 8H_2O$ are listed in Table III.

Spedding, Hamlin and Nutting[15] have recently measured the absorption spectra of $Nd_2(SO_4)_3 \cdot 8H_2O$ and interpret their photographs to indicate that there are two electronic energy levels removed 77 cm^{-1} and 260 cm^{-1} from the basic energy state. The ground state of Nd^{+++} is $^4I_{9/2}$ ($L=6$). For such states Kramers[16] and Bethe[17] have shown that in the presence of the sort of electric fields existing in the crystals, the ten components of this state will split into a double level and two different quadruple levels. The double level will possess a lower energy than the quadrupole levels. For a more detailed discussion of these effects reference should be made to the theoretical article of Penney and Schlapp.[13] Substitution of the statistical weights $p=2$, 4 and 4 and the energies 77 and 260 cm^{-1}, respectively, into Eq. (I) gives the heat capacity of the electrons as necessitated by such a distribution of the energy states. These values are compared with the experimental values in Fig. 2.

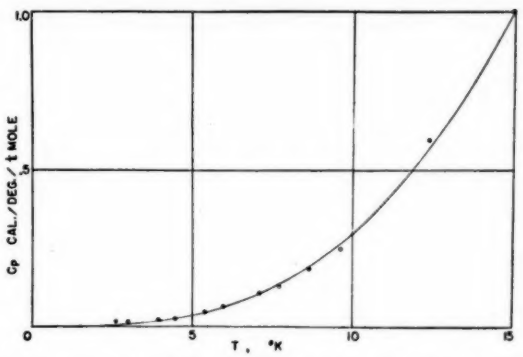

FIG. 3. Dots, $Sm_2(SO_4)_3 \cdot 8H_2O$; circles, $Nd_2(SO_4)_3 \cdot 8H_2O$; straight line, values of $0.0003T^2$.

TABLE II. *Heat capacity of 360.42 g (½ mole) $Nd_2(SO_4)_3 \cdot 8H_2O$.*

T_{Av} °K	ΔT	C_p per ½ mole in cal./deg.
3.00	0.63	0.015
4.47	1.18	.025
5.97	1.30	.065
7.71	1.80	.130
9.62	1.93	.250
11.63	2.36	.565
14.20	2.97	1.12
17.35	2.33	1.89
20.53	2.98	2.90
24.61	5.01	5.93
29.12	3.96	6.41
32.99	3.95	7.67
37.21	4.54	9.75

TABLE III. *Electronic heat capacity of 360.42 g (½ mole) $Nd_2(SO_4)_3 \cdot 8H_2O$ (from direct heat capacity measurements).*

T_{Av} °K	C_v cal./deg./½ mole salt
3.00	0.0
4.47	0.0
5.97	0.0
7.71	0.0
9.62	0.0
11.63	0.07
14.20	0.20
17.35	0.36
20.53	0.58
24.61	2.41
29.12	1.38
32.99	1.28
37.21	1.83

[14] Simon and Kurti, Naturwiss. **21**, 178 (1933); Zeits. f. physik. Chemie **B20**, 305 (1933).
[15] Spedding, Phys. Rev. **50**, 574 (1936) and Spedding, Hamlin and Nutting, J. Chem. Phys. **5**, 192 (1937).
[16] Kramers, Proc. Amst. Acad. **33**, 959 (1930).
[17] Bethe, Ann. d. Physik **3**, 133 (1929); Zeits. f. Physik **60**, 218 (1930).

The presence or absence of the states at 260 cm^{-1} has little effect on the heat capacity up to 40°K. Consequently the experimental results are actually only a test of the presence of the energy level at 77 cm^{-1} and the assumption that its statistical weight is twice that of the lowest level. The agreement between the direct experimental heat capacity values and those calculated from spectroscopic data is conducive to acceptance of the interpretation given. An assumption that the statistical weights are equal leads to a radical disagreement. The fact, shown by the measurements, that the heat capacity curve of the salt between 3° and 10°K does not depart appreciably from the simple type of pattern produced by the elastic vibrations in the crystal lattice shows that the separation of the two lowest states (double-level) must be less than 1 cm^{-1}.

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On the Role of Dipole-Dipole Coupling in Dielectric Media

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The mathematical treatment of dipole-dipole coupling in my previous article on magnetism applies with but little modification to the electric case. Because of fluctuation effects, the use of the usual Lorentz local field $E+4\pi P/3$ and of the Clausius-Mossotti formula cannot be justified except as a first approximation valid at low density. Consequently one need not accept the C-M prediction that polar liquids should exhibit the electric analogue of ferromagnetism. A Gaussian approximation, or better still, a formula based on Onsager's field would never allow ferromagnetism. Consequently the hypothesis of hindered rotation, as in the theories of Fowler and Debye, may not be necessary to explain the absence of spontaneous polarization, as well as the non-occurrence of much saturation curvature in strong applied fields. It is a weakness of their theory that this hypothesis cannot consistently be employed both for such purposes and to explain discontinuities in dielectric constants and specific heats at lower temperatures (e.g., 100° in HCl). It is surprising that the Clausius-Mossotti formula works so exceedingly well as it does in nonpolar liquids, since it is theoretically valid at high densities only for an artificial model of harmonic oscillators which cannot be regarded as an accurate representation of the induced polarization. The calculations of Kirkwood on the translational fluctuation effect, causing deviations from the C-M expression in gases, are extended to include polar molecules, and agree adequately with recent measurements of Keyes and collaborators on NH_3.

1. INTRODUCTION——ADAPTATION OF OUR PREVIOUS CALCULATIONS TO THE ELECTRIC CASE

IN an article in a preceding issue of this journal (henceforth called l.c.[1]), I considered the influence of dipole-dipole coupling on the paramagnetic susceptibility, and found it unimportant except at very low temperatures. On the other hand, due to the fact that the dipole moment, expressed in appropriate units, is usually much larger in the electric than in the magnetic case, this coupling affects the dielectric constant of a polar substance even at room temperatures. The calculations of l.c. apply to electric susceptibilities with but little change. There is also the corresponding specific heat which is due to electric dipole-dipole coupling, but which we shall not discuss explicitly since the bearing on experiment is meager owing to overshadowing by other specific heats. In the particular case of susceptibility due entirely to permanent dipoles, the detailed development of the partition function in $1/T$ is almost identical with that given in Sections 3–4 of l.c. if $g^2\beta^2J(J+1)$ everywhere be replaced by the square of the permanent dipole moment μ of the molecule. There is, however, the simplification that the various components of electric dipole moment commute in matrix multiplication. Hence the noncommutation correction factor x given in (55) of my previous paper[1] is replaced by unity. Also the exchange terms involving the v's are to be suppressed, as exchange coupling does not have a simple aligning effect on the electric moment. This statement does not

[1] J. H. Van Vleck, J. Chem. Physics **5**, 320 (1937); referred to throughout as l.c. In Eq. (57), z should be replaced by z'.

mean that ultimately the exchange forces cannot affect the orientation of the moment, but this influence will be at such small distances that even electrostatic forces cannot be represented by a dipole-dipole potential. In other words, at too great concentrations higher order poles, with exchange ramifications, can come into play. The problem then becomes one of hopeless complexity, involving what Fowler calls "cooperative phenomena," and we must content ourselves with the consideration of ordinary dipole-dipole coupling.

As compared with the magnetic case perhaps the most important difference of all is in the practical definition of the susceptibility. We saw that in magnetic measurements the "experimental susceptibility" was the ratio of moment to the field strength *before* insertion of the test body. However, in determinations of dielectric constants, the drop of potential across the test body is recorded, and so the mean or macroscopic field E actually inside the specimen is measured directly. The experimental susceptibility is conveniently defined as the ratio of the polarization P per unit volume to E and is the same as the theoretical definition of the susceptibility in electromagnetic theory. There is consequently no need of an analogue of a demagnetizing correction and if the body is isotropic with evenly spaced similar atoms, the local field is simply $E+4\pi P/3$, where E is known. Hence in adapting the calculations of l.c. we can replace H_0 by E and take Φ everywhere equal to $4\pi/3$ since the part of (43) of l.c. arising from demagnetizing effects is to be omitted. This is an obvious improvement, as Φ then ceases to be shape dependent.

Clausius-Mossotti formula. According to the usual Lorentz theory, the effect of dipole-dipole coupling is equivalent to taking the local field to be $E+4gP/3$. Then

$$(\epsilon-1)E/4\pi=P=N\gamma(E+4\pi P/3), \qquad (1)$$

where γ is the polarizability per atom and N is the number of atoms per cc. One thus has immediately the Clausius-Mossotti formula

$$\frac{M}{\rho}\frac{\epsilon-1}{\epsilon+2}=\frac{4\pi L\gamma}{3}. \qquad (2)$$

The Avogadro number is denoted by L, and M is the molecular weight. The important feature of (2) is that its right side is a constant independent of the density ρ. The usual Langevin-Debye formula gives $\gamma=\alpha+\mu^2/3kT$, where μ is the permanent dipole moment of a molecule, and α represents the effect of the induced polarization. Thus Eq. (1) can also be written

$$\epsilon-1=3q\theta/(T-q\theta), \qquad (3)$$

where

$$\theta=4\pi N\mu^2/9k=4\pi\tau/9, \qquad q=1+(3\alpha kT/\mu^2). \qquad (4)$$

In polar media, most of the electric susceptibility arises from the permanent dipoles, and the factor q embodying the effect of induced polarization may be replaced by unity without serious error.

2. Polar Liquids and Solids

As stressed in l.c., the usual Lorentz derivation[2] of (1) and hence (2, 3) is based on essentially electrostatic methods and consequently cannot be regarded as rigorous. Instead the problem should be treated as one in statistical mechanics. Our previous paper[1] contains, we believe, the first general kinetic derivation of (2) or (3). However, these formulas are obtained only if either: (a) θ is small compared to T so that in the development of the partition function as a series in $1/kT$ only terms of the first order in the dipole-dipole interaction need be retained, or if (b) the results of this first approximation be extrapolated to higher approximations by a procedure which is comparable to assuming that all states of the same crystalline spin have the same energy in the Heisenberg theory of ferromagnetism. The assumption (b) is, however, necessary to yield (2–3) in liquids and solids, where θ is comparable with T, and certainly (b) is not rigorous. If instead of (b) one extrapolates the results of the second approximation by a procedure analogous to using a Gaussian distribution of energies in Heisenberg's theory, one has[3]

[2] Cf. H. A. Lorentz, *The Theory of Electrons*, note 54.

[3] In the case $q=1$ of no induced polarization, Eq. (5) is the same as (56) of l.c. when adapted to the electric case as explained in Section 1. Eq. (5) is also valid when the induced moment is included, provided it is represented by the harmonic oscillator model. The proof of (5) under these conditions is obtained in the following way as a by-product to our analysis of the translational fluctuation effect in Section 5 of the present paper. The expression $2\alpha^{(2)}\chi_0^{-1}kT$

$$\epsilon-1=\frac{3\theta q}{T-\theta q+(9Q\theta^2/16\pi^2T)}. \tag{5}$$

The quantity Q is dimensionless and is defined as

$$Q=2N^{-2}\Sigma_j r_{ij}^{-6}, \tag{6}$$

where r_{ij} is the distance between atoms i and j and the summation is over all atoms j in the crystal. The values of Q are 16.8 and 14.4, respectively, for simple and face-centered cubic lattices, while Q becomes $2(4\pi/3)^2=35.1$ for a continuous distribution analogous to that usually assumed in classical theory. (Cf. Eqs. (20) and (60) of l.c.) Another possible way of extrapolating the second approximation is by means of Onsager's formula[4]

$$\frac{\epsilon-1}{\epsilon+2}-4\pi\left(\frac{N\alpha}{3}+\frac{N\mu^2}{9kT}\right)=(f-1)\frac{4\pi N\mu^2}{9kT}, \tag{7}$$

$$\text{with}\quad f=\frac{3\epsilon(n^2+2)}{(2\epsilon+n^2)(\epsilon+2)},\quad \frac{n^2-1}{n^2+2}=\frac{4\pi N\alpha}{3}. \tag{7a}$$

Onsager obtained his formula on the ground that the Lorentz field is not really the best electrostatic model and ought to be modified to allow for the "back action" of the medium on the dielectric. This distinction is perhaps most easily comprehended by consulting Fig. 1 of l.c. In the Onsager model as we use it, the cavity is supposed to equal the mean molecular volume in size. In Fig. 1, it is drawn the same size in the Lorentz picture, as is allowable since (except for the Onsager reaction effect) the field at the center of a cavity in a uniformly polarized medium is independent of its diameter. For purposes of deriving the Lorentz formula, the cavity is usually considered very much larger, so as to embrace a considerable number of molecules, whose effect on the central molecule is supposed to vanish on the average if there is spherical symmetry. The gist of the Onsager modification is that the latter supposition is not legitimate in a *polar* medium because of correlations between the orientations of adjacent dipoles, whose effect is embodied in his "reaction field." This reaction term depends on the size of the cavity, and only by taking it equal to the mean molecular volume do his formulas reduce to the Lorentz or Clausius-Mossotti expressions in the nonpolar case.

There is apparently no easy way to decide by simple physical considerations whether the Onsager or Lorentz model is really the better. At first sight, the Onsager method seems preferable since it allows the surroundings of a molecule to adjust themselves to the latter's rotation. However, the average period of a molecule's free rotation is short compared with the relaxation time of a polar dielectric, as determined by Debye's well-known theory of dispersion at radio frequencies.[5] If the rotations are thus so rapid that other molecules cannot follow them at all, the Lorentz model should be the truer picture.[6] In the case of molecules of the HCl type, which have only two rotational degrees of freedom, this objection to the Onsager method may be disposed of by noting that the only contribution to the dielectric constant comes[7] from the irrotational state $J=0$. With molecules of the H_2O type, which have three rotational degrees of freedom, and which comprise most polar molecules, all the states are effective. The largest individual contributions, to be sure, come from the states with low rotational frequencies for the dipole moment[8] but it is not clear whether the resulting weighting of the low states is sufficient to dispose of the difficulty.

In view of this uncertainty, it is particularly interesting to compare the Onsager formula with the one obtained by the method of partition functions,—a very different procedure, which is exact as far as it goes, but in which it is feasible to compute only the first few terms in a series development in the dipole-dipole interaction. It was shown in Section 5 of l.c. that both methods

in (82) of l.c. represents the effect of the term α in (6^8) of l.c. (type $i=k, j=l$) and so must equal the quantity $\lambda P_0/V$ calculated in our later Section 5 when Q is specialized to $32\pi^2/9$ in (5), when only terms of order $1/a^3$ are retained in (20), and when $4\pi a^3/3$ is taken equal to $1/N=V/L$. Namely, with these restrictions it is easily seen that there is no distinction from a formal standpoint between a calculation with the continuum model of regularly spaced atoms, and one on the translational fluctuation effect. The result (5) then follows from (82) of l.c. on using the value of λP_0 given in (20) of the present paper and on noting that $\alpha^{(2)}$ is proportional to Q.

[4] L. Onsager, J. Am. Chem. Soc. **58**, 1486 (1936).

[5] P. Debye, *Polar Molecules*, Chap. V.

[6] I am indebted to Professor Hans Mueller for pointing out this difficulty in the Onsager model.

[7] Cf., for instance, R. de L. Kronig, Proc. Nat. Acad. Sci. **12**, 488 (1926).

[8] See Kronig, ibid. **12**, 611 (1926).

agree to the second approximation in the dipole-dipole interaction,—one order more than with the Lorentz relation. The proof was given only for permanent dipoles, but is unimpaired by inclusion of the induced polarization if the latter is represented by the usual artifice of harmonic oscillators. Namely, to the approximation in question,[9] $f-1$ equals $-32\pi^2N^2\mu^4q/81k^2T^2$, and then (5) and (7) are equivalent to terms in μ^6 if $Q=2(4\pi/3)^2$. In any case, as stressed at the very end of l.c., such agreement is secured only by using this value of Q corresponding to a continuum. A natural way of empirically modifying (7) to conform to other more real values of Q is to multiply the right side of (7) by a factor $(9/32\pi^2)Q$.

There is no doubt that the Onsager formula (7) works much better than the Gaussian one (5). According to (5), the dielectric constant can never exceed 4.7, as one sees by minimizing the denominator of (5) with $q=1$. The assumption $q=1$ is legitimate, as induced polarization is usually subordinate in polar media. Actually ϵ for H_2O is around 80, while even HCl has values of ϵ as high as 17. Furthermore Eq. (5) predicts that $d\epsilon/dT>0$ when $T<3\theta Q^{\frac{1}{3}}/4\pi$; e.g., when $T<.91\theta$ if $Q=14.4$. In reality the dielectric constant continues to increase with decreasing temperature down to values of T far less than θ (e.g. to 273°K in H_2O, whereas $\theta=1200°$). On the other hand, Onsager shows that for suitable values of n, his formula (7) is for large ϵ nearly the same as Wyman's[10] empirical relation $4\pi N\gamma/3=(\epsilon+1)/8.5$, which fits quite well a considerable body of experimental data. This resemblance to Wyman's formula, would, however, be lost if (7) were modified as suggested above to conform to actual values of Q, and we believe that it is over-optimistic to attach much fundamental significance to quantitative fitting of the unmodified formula (7) to experimental measurements on polar liquids. Nevertheless, (7) does appear to have the proper qualitative trend away from the Clausius-Mossotti formula. Namely, if either (5) or (7) is used, (2) ceases to be valid. Now it is well known that the Clausius-Mossotti relation (2) is not obeyed in polar liquids and solids. The difficulties are shown strikingly if we use (3), which is essentially equivalent to (2), and neglect induced polarization by taking $q=1$. Eq. (3) then predicts that the dielectric constant becomes infinite at a critical temperature θ. This behavior we shall refer to as a $4\pi/3$ catastrophe, since it arises from the term $4\pi P/3$ in the local field, without which the denominator of (3) would be simply T. Of course the dielectric constant would not really become infinite, as it is necessary to consider saturation corrections when T is below θ. The physical meaning of the $4\pi/3$ catastrophe, if it occurs, is thus that there is a critical temperature below which there is the electric analogue of ferromagnetism—i.e., saturation, hysteresis, remanence, etc. Actually, such a behavior is practically unknown, being confined largely to Rochelle salt, even if T is reduced to a small fraction of the values of θ given by (4). For example, though θ is 260° for HCl and 1200°K for H_2O, no spontaneous polarization is ever observed for these substances, even at the temperature of liquid air. According to either the Gaussian formula (5) or the Onsager expression (7), spontaneous electric polarization is impossible. The case of Rochelle salt must be regarded as special, since this is an anisotropic body for which the factor Φ in the customary local field $E+\Phi P$ can be much larger than $4\pi/3$ along certain directions. In fact, inspection of Fowler's model[11] for Rochelle salt shows that it is quite possible to construct values of Φ considerably greater even than the minimum value[12] 8.2 which is required for spontaneous polarization with a Gaussian calculation and which is probably an over-estimate. It is thus doubtful whether a $4\pi/3$ catastrophe should occur in an isotropic medium.

One thing is certain, and that is that the energy of a collection of dipoles is not rigorously a minimum when they

[9] This value of $f-1$ follows on substituting in (7a) the approximate value (3) of ϵ and disregarding cubes of μ^2 or α. This substitution is legitimate, since $f-1$ need only be computed to the approximation μ^4 in evaluating (7) to μ^6. In comparing (5) and (7), the right side of (5) may be considered equivalent to $3q\theta[1-(9Q\theta^2/16\pi^2T^2)]/(T-q\theta)$ since (5) is only rigorous to θ^3 or μ^6. Accuracy to μ^6 represents a second approximation in the dipole-dipole interaction, since even without this coupling the susceptibility involves μ^2, and since the dipole-dipole potential is proportional to the product of two elementary moments, i.e., to μ^2.

[10] J. Wyman, Jr., J. Am. Chem. Soc. **58**, 1482 (1936).

[11] R. H. Fowler, Proc. Roy. Soc. **149A**, 1 (1935).

[12] Cf. remarks following (57) of l.c.

are all parallel. The fact that the total resultant moment P is not a constant of the motion when the interaction between the elementary dipoles is of the true dipole-dipole rather than exchange type immediately shows that mutually parallel orientation cannot give an exact extremum of energy. Instead the wave function for the deepest state will be a linear combination compounded from various possible eigenvalues of P. Of course, this argument would not preclude the possibility that large values of P are dominant in the linear combination, and then one would have a quasi-ferromagnetic condition. With a simple cubic arrangement it seems much more probable that actually the low values of P are dominant. Indeed an elementary classical calculation shows that lower values of the energy than for parallel alignment are obtained when the dipoles are arranged in parallel strings, such that along a string the dipoles all point the same way, but with the directions of the dipoles opposite in adjacent strings; thus: $\rightleftarrows\rightleftarrows\rightleftarrows$. An arrangement of this type gives an energy $-2.7N^2\mu^2$ for a simple cubic lattice, as compared with $-\frac{1}{2}(4\pi/3)N^2\mu^2 = -2.1N^2\mu^2$ for parallel alignment along a long slab (the most favorable case). With the body-centered and face-centered lattices, however, the coefficient -2.7 is replaced by 0 and $+1.9$, respectively, so that the parallel configuration gives deeper energy than alternating strings.[13] This result is, of course, inconclusive because there are many other conceivable nonferromagnetic arrangements besides alternating strings. Still, it is perhaps significant that in the alum salts in which Kürti and Simon report some evidence of ferromagnetism due to dipole-dipole coupling (cf. end of Section 3) the paramagnetic ions are spaced on a face-centered rather than simple cubic lattice. On the other hand, solid hydrogen chloride, which fails to exhibit the electric analogue of ferromagnetism, also has a face-centered lattice. With Fowler's model of Rochelle salt, which is anisotropic and which has the distance between strings considerably larger than the separation of atoms along a string, it seems reasonably clear that much the lowest energy is obtained when the dipoles are all practically parallel. This situation, of course, accords with the known spontaneous polarization of Rochelle salt exhibited along certain directions.

In any event, the calculation of the states of low energy is a far more complicated affair with our dipole-dipole forces than for ordinary exchange or ferromagnetic coupling, where the mutual energy of two dipoles does not depend on how they are oriented relative to their connecting line. Approximation by means of the Lorentz formula, however, does not bring out at all the essential differences between the two cases, as the Lorentz local field differs from the Weiss-Heisenberg one only in the proportionality factor. If there are really any remanence phenomena due to dipole-dipole coupling, they may well be quite different in character than for ordinary ferromagnetic media.

[13] These coefficients have been computed for me by Dr. M. H. Hebb. The zero value for the body-centered lattice is also noted by Fröhlich, Proc. Roy. Soc. **158A**, 97 (1937). In the face-centered case, if the strings are along the 110 rather than 100 axis, the coefficient is reduced somewhat from 1.9, but still remains greater than -2.1.

3. Relation to the Fowler-Debye Theory

The preceding considerations have an interesting bearing on the theory of the dielectric constant of polar liquids and solids developed independently by Fowler[11] and by Debye.[14] To explain the absence of spontaneous electric polarization, they postulate some mechanism in the solids or liquids which can "congeal" the dipoles, so that they are not free to orient, and the susceptibility has in consequence a value much lower than that given by the usual Langevin-Debye formula. It is to be understood throughout that the word "congealing," as we use it, relates to the suppression of free rotation, and does not necessarily have anything to do with the passage from the liquid to the solid state, since the melting point may be quite different from the critical temperature at which free rotation is acquired. In the case of Rochelle salt, which is highly anisotropic and is unusual in exhibiting the electric analogue of ferromagnetism, the hindered rotation suggested by Fowler seems necessary to explain why its spontaneous polarization disappears when the temperature is reduced sufficiently. A different situation, however, is presented by isotropic materials. We have seen that it is very questionable whether an isotropic dielectric body can ever acquire spontaneous polarization simply in virtue of dipole-dipole coupling. If the $4\pi/3$ catastrophe does not exist, it is clearly not necessary to introduce the hypothesis of hindered rotation to explain its non-occurrence.

Instructive evidence is presented by the hydrogen halides, which appears to have been generally overlooked, and which suggests that hindered rotation is not required to prevent spontaneous electric polarization. On the basis of (4) one calculates that the Curie point θ for HCl is about 260°K for HCl, and about 120° for HBr. The absence of saturation can scarcely be blamed on any "congealing" of the dipoles, since a $4\pi/3$ catastrophe is avoided with the Clausius-Mossotti formula only if θ is less than the congealing temperature and since it is generally regarded as known from other evidence (specific heats, etc.) that the transition temperatures at

[14] P. Debye, Physik. Zeits. **36**, 100 (1935).

which free rotation is suppressed are,[15] respectively, 100° and 90° for HCl and HBr. At these temperatures there are large discontinuities in the dielectric constant, which have been correlated by Pauling,[15] and others with the cessation of free rotation. One cannot invoke the congealing of the dipoles to explain the absence of spontaneous polarization over the interval 100–260° in HCl or 90–120° in HBr, and at the same time suppose that sudden loss of free rotation explains anomalies at 100° and 90° respectively. It appears probable that the latter is the correct use. Therefore it seems natural to assume that the absence of spontaneous polarization is to be attributed simply to the inadequacy of the ordinary Lorentz local field, which does not take sufficient cognizance of the fluctuations in the interatomic forces due to variable alignment of the dipoles surrounding a given dipole. Such fluctuations are implicitly involved in the higher approximations in the method of partition functions, while the Onsager model allows for them through his "reaction field," as well as in the main ("direct") part of the field through the redistribution of lines of force due to the existence of the cavity (cf. Fig. 1 of l.c.). Now, as already stated, neither Eq. (5) based on a Gaussian extrapolation of a statistical calculation nor Eq. (7) derived from the Onsager theory ever allows spontaneous polarization. Very likely (5) goes too far, as any Gaussian calculation tends to over-estimate the influence of fluctuations in suppressing saturation phenomena. However, to explain the non-occurrence of a $4\pi/3$ catastrophe in HCl, it is only necessary to suppose that the fluctuation effects make the critical temperature for spontaneous polarization very much lower than that given by (3).[16] In the case of the Heisenberg theory of ferromagnetism, it would be difficult to believe that the Curie temperature given by a nonspreading assumption, comparable to (4) is in error by a factor so large as $2.6=260/100°$, as we would have it in the case of HCl. However, it was shown in Section 5 of l.c. that the fluctuation effects are much more important for dipole-dipole than exchange coupling, and the resulting modification of the Curie temperature correspondingly larger.

The situation in H_2O, CH_2O_2, etc. is less clear than in the hydrogen halides. Large discontinuities in the dielectric constant in H_2O occur at the melting point, unlike the cases of HCl, HBr. If consequently the melting point is accepted as the critical congealing temperature for the free rotation, one has again the difficulty that this temperature is much less than the critical temperature given by (4), so that hindered rotation would not prevent the $4\pi/3$ catastrophe. Hence Fowler assumes somewhat artificially that the dipoles are partially congealed even at the boiling point, enough to prevent spontaneous polarization, and that there is additional congealing at the melting point. The assumption of two real critical congealing temperatures is obviously not attractive. However, the interesting question arises as to whether there may not be some tautology between his model and our fluctuation effects, or in other words how much of the apparent congealing envisaged in the F-D theory may be in part a manifestation of the dipole-dipole potential, rather than true hindered rotation of the Pauling type due presumably to short range forces, e.g., higher order poles, not covered by our calculations with dipole-dipole coupling.

We have based all our discussion so far on the part of l.c. corresponding to atoms which are free except for dipole-dipole coupling. One therefore inquires whether the short-range forces might not be represented by superposing a crystalline field, as in Section 6 of l.c. Unfortunately a simple calculation shows that in classical theory crystalline fields which have a center of symmetry do not modify the dielectric constant if they are distributed at random.[17] In quantum mechanics

[15] L. Pauling, Phys. Rev. **36**, 430 (1930); cf. also the related experimental work on the hydrogen halides by R. M. Cone, G. H. Denison and J. D. Kemp, J. Amer. Chem. Soc. **53**, 1278 (1931) and by C P. Smyth and C. S. Hitchcock, ibid. **55**, 1830 (1933).

[16] If, as suggested after (7), the right side of (7) is reduced by a factor $9Q/32\pi^2$, the resulting critical Curie temperature is $T_c=\theta(q-9Q/32\pi^2)$. If then one uses the value 14.4 of Q appropriate to a face-centered lattice, such as is found in solid HCl, the resulting value of T_c is 106° (taking $q=1$). The difficulty regarding spontaneous polarization thus reappears, since other evidence indicates that free rotation is destroyed only below 100°. Quantitative accuracy, however, is not claimed for our proposed modification of (7).

[17] See, for instance, H. Mueller, Phys. Rev. **50**, 547 (1936). In this very interesting paper, Mueller shows that even symmetric potentials can influence the dielectric constant in case the Lorentz factor Φ depends on direction

this result is not rigorously true, but at ordinary temperatures the spacing of rotational energy levels is sufficiently close that the classical procedure represents a good approximation. If one utilizes fields without a center of symmetry, one has a dissymmetry of a type which is suggestive of dipole-dipole coupling, especially since Fowler has his unsymmetrical fields fade out when the polarization of the medium diminishes (his "cooperative" effect).

Saturation. What has previously seemed one of the most attractive arguments in favor of the Debye-Fowler theory is furnished by Debye's calculation[18] of saturation under the hypothesis of hindered rotation. Namely, in very strong applied fields the dielectric constant ceases to be independent of field strength. At the voltage gradients obtainable experimentally, the deviation $\Delta\epsilon$ from the ordinary value ϵ_0 for weak fields is a quadratic function of the field strength, so that

$$D/E=1+4\pi P/E=\epsilon_0+\Delta\epsilon=\epsilon_0+aE^2. \quad (8)$$

If it is assumed that dipole-dipole interaction can be represented by proper choice of a local field E_{loc} and if induced polarization is neglected then the polarization per unit volume is given by

$$P=N\left(\frac{\mu^2}{3kT}E_{\text{loc}}-\frac{\mu^4}{45k^3T^3}E_{\text{loc}}{}^3\right). \quad (9)$$

Eq. (9) is merely the conventional Langevin formula inclusive of the terms corresponding to incipient saturation. If the usual Lorentz local field is employed, the resulting value of the saturation correction is

$$\Delta\epsilon=-4\pi(\tfrac{1}{3}\epsilon_0+\tfrac{2}{3})^4(N\mu^4/45k^3T^3)E^2, \quad (10)$$

as is seen setting $E_{\text{loc}}=E+4\pi P/3$ in (9), substituting the value (8) of P/E and solving for a with neglect of fourth powers of E. At a field of 100,000 volts/cm., the value of $\Delta\epsilon/\epsilon$ calculated from (10) for water (where $\epsilon=80$, $\mu=1.84\times10^{-18}$) is -3.87, whereas Malsch's[19] experimental value is only -1.1×10^{-3}. To account for this discrepancy in order of magnitude, Debye introduces hindered rotation. As already emphasized, it is necessary to assume that the crystalline field is unidirectional rather than with a center of symmetry. Debye then calculates the factors R and R^* by which the first and second terms of (9) are reduced. We omit repeating the explicit formulas here. Using in R^* the value of the hindering field obtained from R, he calculates a value of $\Delta\epsilon/\epsilon$ which agrees almost perfectly with the experimental determination by Malsch.

In our opinion, however, the agreement thus achieved ceases to be impressive, or an argument for assuming hindered rotation (unless construed as tautological with dipole-dipole coupling) when it is remembered that the Lorentz field is not rigorous. If instead we use in (9) the Onsager field, *viz.*

$$E_{\text{loc}}=[3D/(2D+E)]E, \quad (11)$$

then in the same way as (10) was previously obtained, we find that with free rotation

$$\Delta\epsilon=-4\pi\left(\frac{N\mu^4}{45k^3T^3}\right)\left[\frac{27\epsilon_0{}^4}{(2\epsilon_0{}^2+1)(2\epsilon_0+1)^2}\right]E^2. \quad (12)$$

Only the "direct" part of the local field is included in (11), as the reaction portion has no effect on molecular orientation. The value of $\Delta\epsilon/\epsilon$ calculated from (12) at 100,000 volts per cm is -2.4×10^{-5}. The fact that this is considerably lower in magnitude than Malsch's experimental value -1.1×10^{-3} need not give concern. The point is that the preposterously high value of $\Delta\epsilon/\epsilon$ given by the Lorentz field is entirely avoided, and it is not necessary to introduce hindered rotation to suppress excessive saturation curvature. The absence of quantitative agreement is not surprising, as Onsager himself states formula (11) "is not in general applicable to strong fields, i.e., saturation; because its derivation involves the assumption of an isotropic environment." This observation, however, applies mainly to nearly complete rather than to incipient saturation such as we are studying. We believe that the Onsager model still has at least

and so differs from $4\pi/3$. This effect may well be important in liquids with marked cybotatic structure, where the molecules tend to arrange themselves in locally anisotropic regions. Another possibility is that if in a cybotatic group the molecules have the alternating string arrangement mentioned at the end of Section 2, an unsymmetrical potential of the Fowler-Debye type may be a rough way of allowing for the increase in energy attendant to reversing a dipole against the ordinary dipole-dipole forces. These considerations obviously have no bearing in the case of solid HCl above 100°, which has a face-centered cubic lattice and so is highly isotropic.

[18] P. Debye, Physik. Zeits. **36**, 193 (1935).

[19] J. Malsch, Physik. Zeits. **30**, 837 (1929).

qualitative meaning since its vital feature, that at high polarizations the directive part of the local field is smaller than the Lorentz expression, is very relevant for all calculations on saturation. The fact that $\Delta\epsilon/\epsilon$ is larger experimentally than the value given by (12) is in line with our observation that the Onsager model demands a higher value of the quantity Q defined in (6) than corresponds to actual discrete arrangements and so perhaps overaccentuates deviations from the formulas obtained by the conventional Lorentz procedure.

Bearing of recent magnetic experiments. We must mention that new experiments by Kürti, Lainé, and Simon[20] indicate that paramagnetic salts acquire some traces of ferromagnetism at very low temperatures, namely, a feeble remanence and hysteresis. The interesting question arises as to whether this behavior is caused by (a) spontaneous polarization due to dipole-dipole coupling, qualitatively of the type given by the Lorentz local field, (b) exchange forces, or (c) special factors somehow connected with the presence of very low temperatures.

(a) If (a) is the correct explanation, it is very hard to understand why the remanence occurs in paramagnetic but not in dielectric materials. The calculations are, to be sure, not quite the same in the two cases because of the noncommutative terms in the former. However, Eq. (55) of l.c. shows that these terms increase the apparent value of Q, and so work in the wrong direction, tending to suppress saturation in the magnetic rather than electric case. Instead, if hypothesis (a) is accepted, to explain the non-occurrence of spontaneous polarization in dielectrics, it would presumably be necessary to suppose that there is some type of cooperative effect peculiar to the latter and probably somehow associated with the finite length of the dipoles in the electric case. This would be essentially a reversion to the Fowler-Debye hindered rotation, with the attendant difficulties in understanding the behavior of HCl at 100°K.

A crucial experiment which seems to decide against (a) is obtained by investigating the dependence on the shape of the test body. According to (a) any incipient ferromagnetic behavior should be present only in very long specimens. Professor Simon informs the writer that actually the remanence and hysteresis are found even for spherical bodies, to be sure with greatly diminished area in the hysteresis loop, but at a critical entropy and hence presumably at a critical temperature whoch does not differ greatly from that with long samples. If (a) were correct, the Curie point should vary tremendously with shape and vanish for spheres.

(b) It is usually assumed that in paramagnetic salts, in distinction from true ferromagnetic media, the exchange forces can be disregarded because of the large separation between paramagnetic ions. However, Kramers[21] has pointed out that owing to the intervention of the excited states of intermediate, normally diamagnetic atoms, the dependence of the exchange forces upon distance may be less drastic than in the usual exponential type. Hence they may not be negligible. The desired approximate independence of the Curie point of shape can be obtained if the exchange forces are large compared to the dipole-dipole, but then there is the difficulty that the Curie point would be too high, and the deviations from Curie's law too great at helium temperatures. If exchange forces are important only in certain small domains where the atoms are abnormally close together because of crystalline imperfections, this difficulty may disappear, Then, however, it is impossible to understand the great fall in entropy at the remanence temperatures, which indicates that practically all rather than a few atoms are involved in the anomaly, unless one makes the highly improbable assumption that it is a sheer accident that the maximum in specific heat and the acquisition of remanence occur at the same temperature. So all forms of (b) seem to encounter difficulties.

(c) If the remanence and hysteresis are somehow characteristically connected with the very low temperatures found in the magnetic cooling experiments, there is obviously no contradiction with the behavior of dielectrics. Heitler and Teller[22] have shown that there is probably thermodynamic equilibrium between the elementary magnets, but not between them and the lattice vibrations. In dielectrics, on the other hand, we are concerned with much higher temperatures, where the lattice vibrations, as well as the dipole-dipole interaction, can convey energy from one dipole to another. Conceivably certain exceptional dipoles tend to remain "stuck" parallel to the field except as disturbed by vibrational effects, and in this way there might be hysteresis only in the magnetic case. This mechanism, however, yields no insight into the rather large increase in susceptibility concomitant to the appearance of remanence. However, it must be remarked that this increase is nothing like as large as in true ferromagnetic media.

All told, it seems probable that the remanence phenomena observed by Kürti, Lainé, and Simon are not a true $4\pi/3$ catastrophe, and cannot necessarily be construed as evidence that hindered rotation is required to prevent the occurrence of the latter. In any event, their experiments present an interesting and difficult problem for the theoretical physicist, and additional data are greatly to be desired.

4. Nonpolar Liquids or Solids

Much of the evidence for the C-M formula is from gases at high pressures, where $\epsilon-1$ is small compared to unity, so that to a sufficient approximation

$$\frac{M}{\rho}\frac{(\epsilon-1)}{(\epsilon+2)}=\frac{M}{3\rho}(\epsilon-1)[1-\tfrac{1}{3}(\epsilon-1)]. \qquad (13)$$

[20] Kürti, Lainé, and Simon, Comptes rendus, **204**, 675, 754 (1937).

[21] H. A. Kramers, Physica **1**, 182 (1933).

[22] W. Heitler and E. Teller, Proc. Roy. Soc. **155A**, 629 (1936).

However, the C-M expression works remarkably well empirically even for nonpolar liquids. Particularly striking examples are furnished by N_2 and O_2. The C-M ratio; i.e., the left side of (13) has the magnitude 3.869 in O_2 gas, and an almost identical value 3.878 in the liquid, despite the fact that the density differs by a factor over a thousand.[23] The corresponding quantities for N_2 are 4.395 and 4.396. Also there is a mass of experimental evidence that even in polar materials the Lorentz-Lorenz ratio, which is similar except that ϵ is replaced by the square of the optical index of refraction, has often nearly equal values in the gaseous and liquid states. We do not treat explicitly the subject of optical rather than static polarizability, but since the optical refractivity arises entirely from induced polarizability, and is nearly equal to the latter's contribution to the dielectric constant, all the difficulties and other considerations which we raise in connection with the Clausius-Mossotti formula in nonpolar materials also apply to the Lorentz-Lorenz expression even in polar media.

At first thought one might attribute the success of the C-M formula for induced polarization to the fact that only one electronic state has an appreciable Boltzmann factor for each atom or molecule. If the unit of structure is molecular rather than atomic, the rotational and vibrational structure of the ground state may be congealed out by the crystalline field in liquids or solids, and anyway is of subordinate importance for induced rather than permanent polarization. Hence one needs to consider only one state for the "crystal" as a whole (i.e., entire liquid or solid) and the need of developing the partition function as a series in $1/kT$ can be avoided by proper choice of origin. However, this simplification alone does not give the C-M formula (2) since actually to include the dipole-dipole coupling rigorously, one must determine accurately the lowest eigenvalue of the whole liquid or solid, obviously a hopeless task. (Mathematically this difficulty is expressed in the fact that in e.g., the second order of approximation, the last term in Eq. (72) of l.c. persists in contributing to the polarization even if we can omit all portions of $kT \log Z$ with powers of T in the denominator.) The local field method is not rigorous, because even without dipole rotation the moment of an atom oscillates due to the motion of the electrons in their orbits, and so the square of the mean field which it exerts is not equal to the mean square. All that one can say in general about the induced polarization is that the Clausius-Mossotti formula should be valid to a degree of approximation comparable to neglecting the difference between the left and right sides of (13). This accuracy, however, is not sufficient to depict the experimental facts, as in e.g., liquid O_2 the left side of (13) has the value 3.878, and the right side 3.774, whereas the experimental deviations from (2) are of the order 0.01 rather than 0.1. It is therefore imperative to find some model which will yield the C-M formula (2) rigorously. We show below in fine print that (2) is obtained to all orders of approximation if each atom is regarded as an isotropic harmonic oscillator.[24] However, such a model cannot be regarded as bearing much resemblance to a real Rutherford atom. It should be possible to find the simplifications in the rigorous general perturbation formulas which make them furnish answers similar to those for the harmonic oscillator. In this connection, the Onsager model, at least in its original form, sheds no additional light, since it implicitly uses the harmonic model, and so yields the C-M formula in the case of induced polarization. We have in mind rather the work of Serber.[25] He showed that the reason why the conventional formulas based on harmonic oscillators work empirically so well in the Kerr effect and in the depolarization of light is that the general quantum-mechanical atom also yields the same formulas if one makes the "centroid" assumption that all the important absorption frequencies of the atom are nearly equal. By

[23] For references, see Zahn and Miles, Phys. Rev. **32**, 502 (1928).

[24] Incidentally the rigorous validity of the Clausius-Mossotti formula for isotropic harmonic oscillators shows that Lorentz's calculation of the local field was entirely correct for the model which he used. The Onsager procedure can represent an improvement only for the part of the polarization arising from permanent dipoles, which Lorentz did not really have in mind. Our doubts as to the C-M formula for systems other than harmonic oscillators are not to be confused with the objections raised by Kronig and Groenewold (Proc. Amst. Acad. **35**, 974, 1932) and by Darwin (Proc. Roy. Soc. **146A**, 17, **151A**, 572, 1934–5). These authors were concerned with conductors, while we are dealing with insulators. Cf. R. H. Fowler, *Statistical Mechanics*, second edition, p. 437ff.

[25] R. Serber, Phys. Rev. **43**, 1003 (1933).

analogy with his work one is thus led to investigate the hypotheses which will make the C-M formula valid at least in the second approximation in the general treatment in Section 6 of l.c. Eq. (82) of l.c. shows that this requires that $2\alpha^{(2)}kT=Q\chi_0^3$. However, detailed examination, of which we omit the details, shows that this condition is not met merely in virtue of a centroid assumption, but requires in addition that the excited states (involved through matrix multiplication contained in perturbation formulas rather than through appreciable Boltzmann factors) have the same polarizability as the ground state, and that the energy states be evenly spaced. Only the harmonic oscillator possesses these characteristics. It must hence be regarded as an unanswered question why the C-M formula works as well as it does in nonpolar liquids. The best that one can do is to say that the harmonic model surely comes closer to representing induced polarization than that due to permanent dipoles, and so the C-M formula should apply more closely to nonpolar than polar liquids, but this argument gives no insight into why it should apply so exactly to the former.

Derivation of the Clausius-Mossotti formula with the harmonic oscillator model. Let the normal coordinates of a given atom j be $\xi_{1j}\cdots\xi_{fj}$ and let $p_{1j}\cdots p_{fj}$ be the corresponding momenta. The z component, for instance, of the electric moment of any given atom will be a linear function $\Sigma_i d_{ij}{}^z\xi_{ij}$ of its normal coordinates. The Hamiltonian function for the totality of atoms in the solid is

$$\mathcal{H}=\Sigma_{ij}\{\tfrac{1}{2}a_i p_{ij}{}^2+\tfrac{1}{2}b_{ij}\xi_{ij}{}^2-E_0 d^z{}_{ij}\xi_{ij}\}+\Sigma_{ij i'j'}C_{ij i'j'}\xi_{ij}\xi_{i'j'}. \quad (14)$$

Here the first term is the kinetic energy, the second the internal potential energy of the various atoms, the third the electric potential due to the applied electric field E_0, which we have supposed directed along the z axis, and the fourth the dipole-dipole energy. Note that E_0 is not the same as E, since E_0 is the field before insertion of the specimen. The explicit value of $C_{ij i'j'}$ is (cf. Eq. (5) of l.c.)

$$C_{ij i'j'}=C_{i'j' ij}=\Sigma_{q,q'=x,y,z}[\delta_{qq'}-3\cos(q,r_{ij})\cos(q',r_{ij})]d_{ij}{}^q d_{i'j'}{}^{q'} \quad (15)$$

The linear terms in ξ_{ij} may be eliminated from (15) by shifting the origins of the ξ_{ij} to new values $\xi_{ij}{}^0$ which are linear in E_0 and are the roots of the simultaneous linear equations

$$b_i\xi_{ij}{}^0+2\Sigma_{i'j'}C_{ij i'j'}\xi^0{}_{i'j'}=E_0 d_{ij}{}^z. \quad (16)$$

The partition function is then

$$Z=\text{spur}\exp(-\mathcal{H}/kT)=Z^0\exp\Gamma E_0{}^2, \quad (17)$$

where Z^0 denotes the partition function for $E_0=0$ and where

$$\Gamma E_0{}^2=\tfrac{1}{2}\Sigma_{ij}b_i\xi_{ij}{}^{0\,2}+\Sigma_{ij i'j'}C_{ij i'j'}\xi_{ij}{}^0\xi_{i'j'}{}^0.$$

The arguments of Z^0 are not the original normal coordinates $\xi_{11}\cdots\xi_{fN}$ and their corresponding momenta, appropriate to free atoms not exposed to external fields. Instead they are new coordinates $\xi_{11}-\xi_{11}{}^0,\cdots,\xi_{fN}-\xi_{fN}{}^0$ which include the shift in origin necessary to eliminate the linear terms from (14). The conjugate momenta are unaffected by this shift. However, the functional form of Z^0 is the same as before application of E_0 and so its numerical value does not depend on E_0; Thus the moment is

$$P=\partial\log Z/\partial E_0=2\Gamma E_0=\Sigma_{ij}d_{ij}{}^z\xi_{ij}{}^0, \quad (18)$$

the final form being obtained by using (16). Now $\Sigma_j d_{ij}{}^z\xi_{ij}{}^0$ is simply the moment possessed by atom j calculated as a problem in pure electrostatics by finding the equilibrium value ξ^0 of each ξ under the simultaneous influence of three types of forces (I) the internal potential energy, (II) the external field, (III) the dipole-dipole interaction. For such a problem the dipole-dipole coupling is equivalent to a suitable local field, e.g., $E+4\pi P/3$ if there is cubic symmetry and if the atoms are isotropic.[26] In fact, this is precisely the way in which one obtains the conventional formulas for the local field. Our derivation differs only that it is by statistical mechanics, inclusive of momentum terms, rather than by electrostatics.

It is perhaps at first sight rather surprising that the result still holds even with our kinetic method, for when the particles oscillate about their equilibrium positions, the mean square field is not the same as the square of the mean field, and so conceivably fluctuation effects might enter. The reason that the latter do not really spoil things is that even with the dipole-dipole coupling, the Hamiltonian function is still a quadratic function of the ξ^0's. Consequently the method of normal coordinates can still be applied provided we take the whole crystal rather than a single atom as the structural unit, and any system representable by normal coordinates always yields (2).

The preceding calculation is perfectly valid in quantum mechanics, where the ξ's and p's are to be regarded as matrices. The ξ^0's are, on the other hand, mere constants ("c numbers," in Dirac's terminology) and so Γ commutes with the rest of the Hamiltonian function, and there are no difficult questions of ordering, etc. We have, in fact, regarded our preceding calculation as quantum mechanical by labeling in (17) the partition function as a spur. Classical language could, of course, be used instead, and then the spur would be replaced by an integral over phase space.

If the oscillators are anisotropic and are not all oriented in the same way, they will vary among themselves both as regards polarizability relative to a given fixed direction and as regards the local field to which they are subject. The displacement from equilibrium position is the product of the polarizability and effective field; and the mean product, which enters in the formula for the dielectric constant, is

[26] For proof that for cubic symmetry the local field with discrete spacings of atoms is sensibly the same as with the continuum assumed by Lorentz, see Ewald, Ann. d. Physik **49**, 1 (1916).

not the same as the product of the means, because of the variations mentioned in the preceding sentence. In other words the approximation (78) of l.c. may not be satisfied. In an interesting paper, Kirkwood[27] has considered the deviations from the C-M formula due to this cause, which he calls a rotational fluctuation effect,—not to be confused with the translational fluctuations discussed in the next section. We prefer to call these deviations a disordering effect, as they appear in the purely electrostatic approximation, which is the basis of Kirkwood's treatment. Stated in other words, they arise when the classical cavities are nonspherical and oriented at random. It is not clear whether the disordering effect or the substitution of a real atom for the harmonic model causes the larger deviations from the C-M formula. Slight departures from this formula are observed experimentally in a few cases in nonpolar liquids, e.g., pentane.[28]

5. Polar Gases—The Translational Fluctuation Effect

The difficulty of poor convergence of the perturbation theory can be avoided by employing gases at high pressures, as then the density is adequate to make the dipole-dipole interaction appreciable, but at the same time sufficiently low to make the higher approximations negligible. It is well known that the Clausius-Mossotti formula is confirmed by a variety of measurements on condensed gases, and is much more successful than the Dale-Gladstone law $(n-1)/\rho=\text{const.}$, which represents a very crude approximation comparable to complete neglect of the second right-hand member of (13). Nevertheless there is definite evidence that if we write

$$\frac{\epsilon-1}{\epsilon+2}V=P_0\left[1+\lambda\frac{P_0}{V}+\omega\left(\frac{P_0}{V}\right)^2+\cdots\right], \quad (19)$$

where P_0 is the "molar polarization" $4\pi L\gamma/3$ (cf. Eq. (2)) and V is the molar volume, the coefficient λ of P/V is not zero as the Clausius-Mossotti formula would demand. Keyes and Kirkwood have shown that the nonvanishing λ arises from what they call a "translational fluctuation effect."[29] The theory developed in l.c. might suggest at first sight that $\lambda=0$ since the deviations from the C-M formula there appeared in the second rather than first approximation in the density. However, this conclusion was on the basis of a regular spacing of atoms, whereas in a gas the atoms continually approach or recede from each other, so that the mean inverse sixth power of the distance of separation is not at all the same as the square of the mean of the inverse cube. Consequently part of what would be a term in V^{-2}, were there regular spacing, is replaced dimensionally by $V^{-1}a^{-3}$, where a is the distance of closest approach of two molecules. The coefficient λ was calculated by Kirkwood for a model consisting of harmonic oscillators or their equivalent. His computations thus apply at most only to nonpolar materials, and it therefore seems advisable to calculate λ for a more general model consisting of molecules having both a permanent dipole moment of magnitude μ and an induced polarization represented by the usual artifice of isotropic harmonic oscillators, whose coefficient of polarizability will be denoted by α. Explicit calculation, of which we give the details in fine print below, shows that

$$\begin{aligned}\lambda P_0=&(8\pi L\alpha^2/9a^3)(3+2y)\\&+(4\pi L\alpha^3/225a^6)(15+10y+y^2)^2(3+y)^{-1}\\&+(4\pi L\alpha^4/225a^9)(15+10y+y^2)\\&\qquad\times(60+60y+8y^2)(3+y)^{-1}+\cdots, \quad (20)\end{aligned}$$

with $y=\mu^2/\alpha kT$. For the nonpolar case $y=0$, Eq. (20) reduces to Kirkwood's expression if we neglect the correction factor $1+(A/3bT)$ which he includes to allow for the van der Waals' attractive forces, and if we retain terms of only the first order in $1/a^3$. In our opinion, his van der Waals' correction is extraneous, as the dipole-dipole attraction is already included to yield (20) as it stands (specifically, via the exponents in the f_{ij} in our later Eq. (24)). Hence it is redundantly counting things twice to include in addition an attractive potential of the inverse sixth power type due to polarization. The deficiencies of the harmonic oscillator model, are, however, so great that it is rather meaningless to argue profoundly over this question. Kirkwood was entirely justified in retaining only terms in $1/a^3$, since in the nonpolar case the higher order members in $1/a^6$, $1/a^9$, etc., are usually quite unimportant. With polar molecules, however, the influence of these higher terms cannot be neglected, although it does seem allowable to neglect $1/a^{12}$ and beyond,

[27] J. G. Kirkwood J. Chem. Phys. **4**, 592 (1936).
[28] W. E. Danforth, Phys. Rev. **38**, 1224 (1931).
[29] F. G. Keyes and J. G. Kirkwood, Phys. Rev. **37**, 202 (1931): a numerical error in this paper is noted by Kirkwood in footnote 6 of reference 27.

at least in ammonia. It is interesting to note that the permanent polarity alone makes no contribution in the first approximation $1/a^3$ since the first member of (20) vanishes when $\alpha=0$, $y\alpha=\mu^2/kT$. Instead, in the polar case, most of the contribution to λ comes from cross terms between the induced and permanent polarization. This situation explains why excessively large values of λ are obtained if one naively attempts to apply Kirkwood's nonpolar formula to the polar case simply by replacing in Kirkwood's formula the induced polarizability by the complete polarizability $\gamma=\alpha+\mu^2/3kT$. As noted by Keyes and Oncley,[30] such a procedure would yield $\lambda=2$ in NH_3. This is the sole polar gas for which measurements of λ are available, and the observed value of λ is only 0.3, of a different order of magnitude. Keyes and Oncley thus suggest empirically that somehow the induced is relatively more effective than the permanent polarization in contributing to λ, and their conjecture is nicely borne out by the theoretical calculations. The value of λ which (20) yields for NH_3 is 0.4. The discrepancy is no greater than the experimental error. Existing measurements over a temperature range are not sufficiently accurate to test the theoretical temperature dependence. Accurate agreement between theory and experiment is not to be expected, because of experimental error and especially because induced polarization cannot be adequately represented by harmonic oscillators, as stressed in the preceding section. The latter fact possibly explains why the observed values of λ are usually larger than the computed ones in nonpolar gases. The opposite trend, however, is found in the polar material NH_3. Another source of error is that the repulsive potential is not actually of the infinitely sudden type demanded by our hard sphere model.

Existing experimental data are inadequate to yield the second coefficient ω in (19). So we shall not assay the theoretical calculation of ω. We may, however, note that the leading term in a development of ω in powers of $1/a^3$ has the value $-15/16$, so that $\omega=-(15/16)+O(1/a^3)+\cdots$. This result was established by Kirkwood for the harmonic oscillator model, but can be shown to hold for the general molecule.[31, 32]

Proof of Eq. (20). For our purposes, it will be an adequate approximation to use classical mechanics.[33] The Hamiltonian function is

$$\mathcal{H}=\tfrac{1}{2}\Sigma_i b_i \mathbf{r}_i^2-E_0\Sigma_i m z_i+\Sigma_{j>i} w_{ij}, \tag{21}$$

where

$$\mathbf{m}_i=\boldsymbol{\mu}_i+e_i\mathbf{r}_i, \quad w_{ij}=r_{ij}^{-3}[\mathbf{m}_i\cdot\mathbf{m}_j-3r_{ij}^{-2}(\mathbf{m}_i\cdot\mathbf{r}_{ij})(m_j\cdot\mathbf{r}_{ij})]. \tag{22}$$

The first term in (21) is the harmonic binding energy, supposed isotropic. The harmonic displacement vector $\mathbf{r}_i$ is not to be confused with the separation $\mathbf{r}_{ij}$ between the centers of atoms i and j. The total moment $\mathbf{m}_i$ of a typical atom i arises from a permanent portion $\boldsymbol{\mu}_i$ and an induced contribution $e_i\mathbf{r}_i$, where e_i is the effective charge associated with the molecular oscillation. The partition function is

$$Z=\int\cdots\int\exp(-\mathcal{H}/kT)dv_1\cdots dv_L d\tau_1\cdots d\tau_L,$$

where $dv_i=r_i^2\sin\theta_i\sin\Theta_i dr_i d\theta_i d\varphi_i d\Theta_i d\Phi_i$ and where Θ, Φ, and θ, φ are the polar coordinates specifying the orientation of the vectors $\boldsymbol{\mu}_i$ and $\mathbf{r}_i$ respectively while $d\tau_i$ is the volume element in which the center of atom i is located. We suppose that there is a gram mole of material, so that there are L molecules in all. It has not been necessary to include either the oscillational or rotational kinetic energy, as this contributes to Z a factor independent of E_0 which is of no importance for our purposes. (The integration over the rotational momenta does, however, contribute a factor $\sin\Theta_i$ in the volume

[30] F. G. Keyes and J. L. Oncley, Chem. Rev. **19**, 195 (1936): based on experimental work by Keyes and Kirkwood, Phys. Rev. **36**, 1570 (1930) and by Uhlig, Kirkwood, and Keyes, J. Chem. Phys. **1**, 155 (1933).

[31] The term in question is shown by Kirkwood to arise from the excluded part of a sum of the type $\Sigma_{(k\neq i)} r_{ij}^{-3}r_{jk}^{-3}$. This part gave rise to the term $Q\chi_0^2$ in (82) of l.c. The latter term, except for proportionality factors independent of the character of the molecule, depends only on the total polarizability quite irrespective of the model. The same property is preserved when the calculations are adapted to translational fluctuations rather than the uniform spacing assumed in l.c., as the modification consists essentially in altering the value of Q. So Kirkwood's factor $-15/16$ is general.

[32] With the general molecule, the leading term in λ equals $2kT\alpha^{(2)}V/\chi_0 P_0$ where $\alpha^{(2)}$ is defined as in Eq. (72) of l.c., provided $\alpha^{(2)}$ is calculated with a haphazard rather than uniform spacing of molecules. Cf. our footnote 3 and Eq. (82) of l.c.

[33] As far as the part due to the permanent moment is concerned, the present calculation shows considerable resemblance to that given by R. M. Fuoss in J. Am. Chem. Soc., **56**, 1031 (1934). However, we use a series development of the exponentials, whereas Fuoss had to resort to the method of steepest descents because he was interested in much higher concentrations (liquids) where the development would not be convergent.

element.) The partition function involves only even powers of E_0, and we only need the approximation E_0^2. In the expansion of the exponential functions, it is not necessary to consider products of the form $w_{ij}w_{jk}$ etc., when $k \neq i$, as such terms are easily seen to first contribute when $1/V^2$ rather than $1/V$ is considered in (19), the situation being similar to that for the second virial coefficient. Thus we may write

$$Z = \int \cdots \int [1+\tfrac{1}{2}E_0^2k^{-2}T^{-2}(\Sigma_i mz_i)^2][1+\Sigma_{k>j}f_{jk}]\Pi_l \exp(-b_l\mathbf{r}_l^2/2kT)dv_l d\tau_l, \tag{23}$$

where

$$f_{ij} = -1+\exp(-w_{ij}/kT). \tag{24}$$

Since the directions of r_{ij} are random, we may replace mz_i^2 by $\frac{1}{3}\mathbf{m}_i^2$, and mz_imz_j by $\frac{1}{3}\mathbf{m}_i\cdot\mathbf{m}_j$. This can be demonstrated explicitly, for instance, by averaging over all directions for r_{ij}. On separating the terms for which l does, or does not equal i or j, and on performing the integration over the purely translational coordinates, Eq. (23) thus becomes

$$Z = (V-b')^L\Omega^L\{[1+\tfrac{1}{2}L^2\int \hat{f}_{ij}dv_{ij}][1+(E_0^2/6k^2T^2)(L-2)\int \mathbf{m}_i^2dv_{ij}] + (E_0^2/3k^2T^2)\int \mathbf{m}_i^2dv_{ij} + (L^2E_0^2/12k^2T^2)\int(\mathbf{m}_i+\mathbf{m}_j)^2\hat{f}_{ij}dv_{ij}\},$$

with the abbreviations

$$b' = 2\pi La^3/3, \quad \Omega = \int \exp(-b_i\mathbf{r}_i^2/2kT)dv_i, \quad dv_{ij} = \exp[-b_i(\mathbf{r}_i^2+\mathbf{r}_j^2)/2kT]dv_idv_j/\Omega^2, \quad \hat{f}_{ij} = (4\pi/V)\int_a^\infty f_{ij}r_{ij}^2dr_{ij}.$$

In performing the translational integration, we have employed the conventional hard sphere model, with distance of closest approach a, and have neglected all but binary encounters. The various atoms are supposed alike in internal structure, so that subscripts do not really need to be attached to b_i, e_i, etc. As L is very large, it has been allowable to take the number of pairs of molecules as $\frac{1}{2}L^2$ rather than the more exact value $\frac{1}{2}L(L-1)$.

$$\int m_i^2dv_{ij} = \mu^2+3\alpha kT \quad (\alpha = e_i^2/b_i).$$

Here α is obviously the same as the usual coefficient of induced polarizability. The product of two integrals with integrands each involving f_{ij} can be disregarded, since their first contribution begins with $1/V^2$ in (19). Thus

$$Z/Z^0 = 1+\tfrac{1}{2}E_0^2Lk^{-2}T^{-2}\{(\tfrac{1}{3}\mu^2+kT\alpha)(1-L\int \hat{f}_{ij}dv_{ij})+\tfrac{1}{2}L\int \tfrac{1}{3}(\mathbf{m}_i+\mathbf{m}_j)^2\hat{f}_{ij}dv_{ij}\},$$

where Z^0 is the partition function in the absence of E_0.

We now develop f_{ij} as an ascending series in w_{ij}. It is convenient to assume a spherically shaped containing vessel, since then the linear terms in w_{ij} make no contribution to Z. The latter is shown either by the general theory of l.c., or the obvious fact that with complete spherical symmetry, which demands a spherical boundary, the average values of the first and second parts of w_{ij} defined in (22) are equal. In this connection, however, we must remember that the field E_0 as we use it, is the external field before insertion of the body, and is the same as $E+4\pi P/3$, where E is the field inside the spherical dielectric. The remarks of section 1 show that our final results will be independent of the shape of the body if they are expressed in terms of E rather than E_0. Thus we find that if we stop with w_{ij}^4 and if we perform the spacial averaging over different relative inclinations of $\mathbf{m}_i$ and $\mathbf{m}_j$

$$Z/Z^0 = 1+\tfrac{1}{2}E_0^2Lk^{-2}T^{-2}\{(\tfrac{1}{3}\mu^2+kT\alpha)+\tfrac{1}{3}L\overline{r_{ij}^{-6}}k^{-2}T^{-2}[\tfrac{1}{3}\langle\mathbf{m}_i^4\rangle_{Av}\langle\mathbf{m}_j^2\rangle_{Av}-(\tfrac{1}{3}\mu^2+\alpha kT)\langle\mathbf{m}_i^2\rangle_{Av}\langle\mathbf{m}_j^2\rangle_{Av}] + L(2/225)\overline{r_{ij}^{-9}}k^{-3}T^{-3}\langle\mathbf{m}_i^4\rangle_{Av}\langle m_j^4\rangle_{Av}+L(1/75)\overline{r_{ij}^{-12}}k^{-4}T^{-4}[\langle\mathbf{m}_i^6\rangle_{Av}\langle\mathbf{m}_j^4\rangle_{Av}-\langle\mathbf{m}_i^4\rangle_{Av}\langle\mathbf{m}_j^4\rangle_{Av}(\mu^2+3\alpha kT)]+\cdots\},$$

where $$\langle\mathbf{m}_i^n\rangle_{Av} = \Omega^{-1}\int \mathbf{m}_i^n \exp(-b_ir_i^2/2kT)dv_i.$$

Evaluation of the integrals gives

$$\langle m_i^4\rangle_{Av} = \langle m_j^4\rangle_{Av} = \mu^4+10\alpha\mu^2kT+15\alpha^2k^2T^2, \quad \langle m_i^6\rangle_{Av} = \mu^6+21\alpha\mu^4kT+105\alpha^2u^2k^2T^2+105\alpha^3k^3T^3,$$

$$\overline{r_{ij}^{-n}} = (4\pi/V)\int_a^\infty r^{-n+2}dr = [4\pi/V(n-3)]a^{-n+3}.$$

Eq. (20) finally follows on remembering that $P = kT\partial\log Z/\partial E_0$, and $\epsilon-1 = 4\pi P/(E_0-4\pi P/3)$.

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Primary Photochemical Processes in Solution

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The effect of an inert solvent on the efficiency of photodissociation processes is discussed. It is shown on theoretical considerations that under the usual experimental conditions a close analogy between reactions in solution and in the gas phase cannot be accounted for by assuming a symmetrical retardation of both the dissociation and recombination processes by the solvent. It is shown experimentally by means of the radioactive indicator method that even in the ideal case of chlorine in carbon tetrachloride the atoms produced in the photodissociation process do not react with the solvent.

IN considering the nature of the primary process in photochemical processes in solution it is customary to assume that the reaction occurring is the same as would be found in a gaseous system. Thus if we are dealing with absorption corresponding to the continuum of one of the halogens we assume that atoms are formed in solution just as they would be in the gas phase. Dickinson[1] has presented a review of a number of reactions which have been studied both in the gas phase and in solution and he has shown that the behavior of such systems is usually in accord with the above assumption. Franck and Rabinowitch,[2] however, have advanced the argument that the quantum yield of such a primary dissociation process must be small on account of a high rate of "primary recombination." They argue that the atoms when first formed are hemmed in by solvent molecules so that they cannot escape from each other and therefore they recombine giving up the dissociation energy to the solvent molecules. An exception to this state of affairs arises if the atoms (or radicals) react with the solvent.[3] Recently Rabinowitch and Wood[4] have described some experiments with a mechanical model which they interpret as confirming these views. It is to be noted, however, that their results can be compared accurately only to reactions in which the atoms or radicals separate with approximately the same kinetic energy as the solvent molecules. This is usually not true of photodissociations but rather we find the parts separating with abnormally high kinetic energies, thus increasing the possibility of forcing their way between the solvent molecules. The close correspondence between the reactions in gaseous and liquid systems as pointed out by Dickinson suggests that for dissociations of this type the primary recombination must be rather small.

In the interpretation of most of the data on chemical reactions we are concerned with the stationary state concentrations of atoms or radicals rather than their specific rates of formation and disappearance. Rabinowitch and Wood[5] have remarked that if we assume that in such experiments only $1/n$ of the absorption processes result in dissociation and at the same time the recombination is reduced to $1/n$ of the gas phase rate then the stationary state is unchanged so it would be possible to observe the correlation mentioned above and yet have an inefficient primary process. Such a symmetrical modification of the dissociation and recombination processes is required by the principle of microscopic reversibility provided the reactions occur reversibly, i.e., if the separating atoms or radicals have the same kinetic energy as those which are recombining. Ordinarily this condition is not fulfilled but instead we find the dissociation process producing atoms with very high kinetic energies. Such atoms have an excellent chance of forcing their way between the solvent molecules or of reacting with the solvent molecules. The net effect would be that the dissociation would be affected less than the recombination process insofar as an inhibiting action of the solvent

[1] Dickinson, Chem. Rev. **17**, 413 (1935).
[2] Franck and Rabinowitch, Trans. Faraday Soc. **30**, 125 (1934).
[3] Franck, Chem. Rev. **17**, 423 (1935).
[4] Rabinowitch and Wood, Trans. Faraday Soc. **32**, 1381 (1936).
[5] Reference 4, p. 547.

molecules is concerned. This would tend to produce higher concentrations of the atoms in solution if it were not for the fact that in solution the atoms can recombine at every collision with each other as there will always be some other molecule present to act as the third body.

The possibility of the atoms or radicals reacting with the solvent certainly exists in some systems but there are many examples of reactions in inert solvents where such a step seems impossible. Thus in reactions involving the absorption of light by iodine or bromine in solution in carbon tetrachloride the reactions of the atoms with the solvent are so markedly endothermic that they can be ruled out even when the atoms have quite high kinetic energies. With chlorine in carbon tetrachloride the possibility of a reaction, such as a chlorine atom adding on one side of the molecule while another chlorine atom leaves the other side, must be considered as the heat of the reaction is zero. The net result of such a process being merely the replacement of one chlorine atom by another it cannot be detected by ordinary chemical means but it can be detected by using the method of radioactive indicators. We have therefore carried out experiments to test this reaction using radioactive chlorine, obtained from Professor E. O. Lawrence, dissolved in carbon tetrachloride.

The essential steps in the experiment consisted of illuminating a solution of chlorine, some of which was radioactive, in carbon tetrachloride, removing the chlorine and testing the carbon tetrachloride for radioactivity. The chlorine was prepared from sodium chloride, which had been activated by the cyclotron, by oxidizing with manganese dioxide in acid solution. The gas was dissolved in carbon tetrachloride which had been washed with sodium hydroxide, dilute sulfuric acid, water, dried with anhydrous sodium sulfate, and distilled (b.p. $76\pm0.1°$). The solution was divided into two parts, one to serve as a control, the other for the illumination. The latter was placed six inches from a quartz mercury arc (220 volt Cooper-Hewitt) with a piece of plate glass between the two to ensure the elimination of all wave-lengths which might affect the carbon tetrachloride. In order to obtain a measure of the effective light intensity two control reactions involving absorption of light in the same spectral region as chlorine in carbon tetrachloride were used. The first was the decomposition of a solution 0.01 M in uranyl nitrate and 0.05 M oxalic acid for which an average quantum yield of 0.6 was assumed.[6] The second was the decomposition of a solution of chlorine in 0.1 M hydrochloric acid for which Allmand[7] gives an average quantum yield at these wave-lengths of 0.05. As the light was not monochromatic it is obviously impossible to obtain an exact check by such methods but these two tests agree within twenty percent in showing that in the course of thirty minutes illumination enough light would be absorbed by the chlorine in the carbon tetrachloride to dissociate all the molecules four times. After such a period of illumination the chlorine was removed from the carbon tetrachloride by shaking with a solution of sodium sulfite. This carbon tetrachloride was compared with the control solution of chlorine in carbon tetrachloride by means of a counter such as has been used in previous work on liquid systems in this laboratory.[8] The liquid which had been given the treatment described above gave a count of 77.4 ± 2.3, a blank run with carbon tetrachloride gave 82.6 ± 2.8, for half-minute intervals. These values were obtained by taking readings with the two liquids alternating in the counter. Then the count for the control solution of chlorine was determined and found to be 256 ± 5. Subtracting 80 as an allowance for the zero of the counter we find 176 ± 6 as the activity due to the chlorine. The mean time for this determination was 38 minutes later than for the tests on the carbon tetrachloride. This is approximately the half-life of radioactive chlorine, therefore before we can compare our results we must multiply our observed activity by two to get the activity which existed at the time of the tests on the carbon tetrachloride. The resulting value is 350 in round numbers. The difference between the treated and untreated samples of carbon tetrachloride was -5.2 ± 4. Such a negative value must be attributed to fluctuations in the zero point as any appreciable amount of

[6] Leighton and Forbes, J. Am. Chem. Soc. **52**, 3139 (1930).
[7] Allmand, Cunliffe and Maddison, J. Chem. Soc. (London) **131**, 165 (1927).
[8] Olson, Libby, Long and Halford, J. Am. Chem. Soc. **58**, 1313 (1936).

interchange involving the radioactive chlorine would give a positive value. Under the circumstances we feel that it is conservative to say that the amount of interchange which occurred is less than that necessary to give a difference of ten in the count. In other words, less than 10/350 or 0.029 of the chlorine reacted. As the total light absorbed was four times that necessary to dissociate all of the chlorine we can say that the quantum yield of the interchange process at room temperature is certainly less than 0.007.

The data which have been presented show that even in the most favorable case, chlorine in carbon tetrachloride, we cannot account for a high efficiency of a photodissociation process by assuming that the dissociation products react with the solvent. In the earlier paragraphs we have shown that the hypothesis that the rates of dissociation and recombination are both reduced by the same factor so that the concentration of atoms in the photostationary state is comparable with that in the absence of a solvent is not tenable under the experimental conditions which have prevailed in most investigations. It seems necessary to assume, therefore, that the primary action of the light on a molecule must be of comparable efficiency in solution and in the gas phase if we have a close correlation between the behaviors of the two systems. The effect predicted by Franck and Rabinowitch should appear if we work with light of such frequency that the energy is just enough to bring about a dissociation. Even under such conditions it will not be observed experimentally unless the reaction mechanism is such that the active intermediates produced by the light are removed by some other reaction than a homogeneous recombination. A search is being made for a suitable reaction.

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The Temperature, Pressure and Volume Coefficients of the Viscosity of Fluids

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Since $(\partial\eta/\partial T)_p$ and $(\partial\eta/\partial T)_V$ are both positive for dilute gases and both are negative for ordinary liquids, they must be zero at some intermediate density. From data in the literature it is shown that these two coefficients do not become zero at the same state of the fluid, but that the former becomes zero at lower densities than does the latter. On this basis any state of a fluid can be placed in one of six categories, or loci, which are characterized by the signs and relative magnitudes of the two viscosity temperature coefficients. By the use of general mathematical equations relating four variables, the signs of the viscosity pressure and viscosity volume coefficients are deduced for the six loci. It is shown that the fluidity and volume of a normal liquid are linearly related for volume changes up to about 10 percent, as both properties are varied with the pressure at constant temperature, i.e., that $(\partial\varphi/\partial V)_T$ is a constant. This is analogous to Batchinski's relation, according to which $(\partial\varphi/\partial V)_p$ is a constant. From data in the literature it is shown that $(\partial\varphi/\partial V)_T$ is about $\frac{3}{5}$ to $\frac{3}{4}$ of $(\partial\varphi/\partial V)_p$, in agreement with relations deduced in this paper.

THE viscosity of a homogenous fluid is a function of the state only, just as are the pressure, temperature, and volume, and any of these four variables is fixed by fixing any two of the others. The commonest equations of state are those involving p, T and V, but formally at least, an equation relating p, T and η could equally well be called an equation of state. The volume pressure and volume temperature coefficients are well known to be negative and positive numbers, respectively, for any phase, gas, liquid or solid. The corresponding coefficients of viscosity are however not so simple nor so well known, for instance the viscosity temperature coefficient is positive for gases and negative for ordinary[1] liquids, but its transition from the one sign to the other has never been investigated.

The following pages discuss all the viscosity coefficients of the four dimensional surface p–T–V–η for all fluid phases from the dilute gas to the highly compressed liquid. The data

[1] The term ordinary liquids will be used in the early part of this paper to mean a liquid below its normal boiling point. Later a more precise definition will be given the term from a viscosity standpoint.

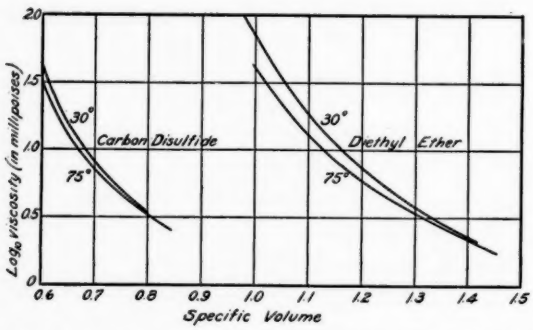

FIG. 1. Log viscosity specific volume isotherms for carbon disulfide and diethyl ether (from Bridgman). This figure is essentially the same as Fig. 8 in Bridgman's paper.

necessary for such an investigation were not available previous to the comprehensive work of Bridgman[2] on the viscosity of liquids under pressure and Stakelbeck's[3] work on the viscosity of carbon dioxide in the critical region.

The discussion can best be begun by considering the viscosity temperature coefficients. It is well known from kinetic theory and experiment that $(\partial\eta/\partial T)_V$ and $(\partial\eta/\partial T)_p$ are equal and positive for dilute[4] gases. It is also well known from experiment that $(\partial\eta/\partial T)_p$ is negative for ordinary liquids. Faust[5] claimed to have shown that $(\partial\eta/\partial T)_V$ was zero for carbon disulfide and ether in the range 0° to 40° and 1 to 3000 atmospheres, but his data show that $(\partial\eta/\partial T)_V$ is in reality a small negative number in both cases. Bridgman's[2] results over a much wider range show definitely that $(\partial\eta/\partial T)_V$ is negative for ordinary liquids, but that it becomes smaller in absolute value as the volume is increased. This is shown in Fig. 1, drawn from Bridgman's data. The largest volumes in the figure are for 75° under the vapor pressure of the liquid at 75°. It appears that the curves will cross and $(\partial\eta/\partial T)_V$ become zero at a volume not much greater than the largest in the figure. It can be concluded from this that the smallest volume at which $(\partial\eta/\partial T)_V=0$ is the volume of the liquid under its own vapor pressure at a temperature probably closer to the normal boiling point than to the critical temperature.

Since $(\partial\eta/\partial T)_V$ and $(\partial\eta/\partial T)_p$ are both positive for dilute gases and both are negative for ordinary liquids, it is obvious that they both decrease algebraically as the volume is decreased, each becoming zero at some intermediate density.

TABLE I. *Viscosity of liquid and gaseous carbon dioxide (from Stakelbeck) (viscosity in millipoises).*

atmos. p \ t°C	0	10	20	30	40
5	0.139	0.142	0.146	0.149	0.157
10	0.143	0.144	0.149	0.151	0.159
15	0.147	0.145	0.151	0.153	0.161
20	0.151	0.149	0.154	0.160	0.167
25	0.155	0.153	0.156	0.160	0.167
30	0.162	0.157	0.159	0.163	0.170
35	0.994	0.162	0.162	0.167	0.174
40	1.042	0.171	0.167	0.171	0.177
45	1.067	0.857	0.174	0.175	0.182
50	1.091	0.897	0.182	0.180	0.187
55	1.111	0.936	0.192	0.187	0.193
60	1.132	0.964	0.728	0.196	0.200
65	1.149	0.990	0.765	0.210	0.208
70	1.167	1.011	0.799	0.228	0.219
75	1.184	1.034	0.829	0.523	0.234
80	1.198	1.056	0.856	0.574	0.260
85	1.211	1.075	0.882	0.619	0.303
90	1.225	1.094	0.906	0.659	0.367
95	1.238	1.112	0.927	0.694	0.436
100	1.249	1.129	0.948	0.727	0.497
105	1.260	1.144	0.967	0.758	0.547
110	1.272	1.159	0.986	0.785	0.588
115	1.283	1.174	1.004	0.812	0.623
Vapor pressure (in atmospheres)					
	34.38	44.41	56.50	71.14	—

TABLE II. *Molal volume of carbon dioxide (from Amagat).*

atmos. p \ t°C	0	10	20	30	40
30	560.0	611.0	—	—	—
35	48.0	489.0	535.0	575.0	—
40	47.6	395.0	442.0	480.5	517.0
45	47.2	52.3	367.0	407.0	442.0
50	47.0	51.3	304.5	347.0	381.0
55	46.7	50.5	246.5	296.0	331.0
60	46.5	49.9	56.8	249.5	288.0
65	46.3	49.4	55.65	205.0	250.0
70	46.1	49.0	54.7	150.5	215.5
75	45.9	48.7	53.8	65.4	183.0
80	45.75	48.4	53.05	62.4	151.5
85	45.6	48.2	52.5	60.6	114.8
90	45.5	48.0	52.0	59.25	84.9
95	45.35	47.8	51.55	58.05	74.0
100	45.2	47.7	51.2	57.1	69.2
105	45.1	47.55	50.9	56.35	66.5
110	44.9	47.4	50.65	55.7	63.8
115	44.8	47.2	50.45	55.1	62.3

[2] Bridgman, Proc. Am. Acad. Arts Sci. **61**, 57 (1925–26).
[3] Stakelbeck, Zeit. ges. Kalte-Industrie **40**, 33 (1933).
[4] The term dilute gas will be used to mean a gas for which the kinetic theory prediction of the pressure independence of viscosity is true.
[5] Faust, Zeits. f. physik. Chemie **86**, 479 (1914).

TABLE III. *The coefficients of viscosity of fluids.*

Locus	State	Temperature Coefficients	Pressure Coefficients	Volume Coefficients
I	Dilute gases	$\left(\frac{\partial\eta}{\partial T}\right)_p +$, $\left(\frac{\partial\eta}{\partial T}\right)_V +$, $\left(\frac{\partial\eta}{\partial T}\right)_p = \left(\frac{\partial\eta}{\partial T}\right)_V$	$\left(\frac{\partial\eta}{\partial p}\right)_T = 0$, $\left(\frac{\partial\eta}{\partial p}\right)_V +$, $\left(\frac{\partial\eta}{\partial p}\right)_T < \left(\frac{\partial\eta}{\partial p}\right)_V$	$\left(\frac{\partial\eta}{\partial V}\right)_T = 0$, $\left(\frac{\partial\eta}{\partial V}\right)_p +$, $\left(\frac{\partial\eta}{\partial V}\right)_T < \left(\frac{\partial\eta}{\partial V}\right)_p$
II	Compressed gases	$\left(\frac{\partial\eta}{\partial T}\right)_p +$, $\left(\frac{\partial\eta}{\partial T}\right)_V +$, $\left(\frac{\partial\eta}{\partial T}\right)_p < \left(\frac{\partial\eta}{\partial T}\right)_V$	$\left(\frac{\partial\eta}{\partial p}\right)_T +$, $\left(\frac{\partial\eta}{\partial p}\right)_V +$, $\left(\frac{\partial\eta}{\partial p}\right)_T < \left(\frac{\partial\eta}{\partial p}\right)_V$	$\left(\frac{\partial\eta}{\partial V}\right)_T -$, $\left(\frac{\partial\eta}{\partial V}\right)_p +$, $\left(\frac{\partial\eta}{\partial V}\right)_T < \left(\frac{\partial\eta}{\partial V}\right)_p$
III		$\left(\frac{\partial\eta}{\partial T}\right)_p = 0$, $\left(\frac{\partial\eta}{\partial T}\right)_V +$, $\left(\frac{\partial\eta}{\partial T}\right)_p < \left(\frac{\partial\eta}{\partial T}\right)_V$	$\left(\frac{\partial\eta}{\partial p}\right)_T +$, $\left(\frac{\partial\eta}{\partial p}\right)_V +$, $\left(\frac{\partial\eta}{\partial p}\right)_T = \left(\frac{\partial\eta}{\partial p}\right)_V$	$\left(\frac{\partial\eta}{\partial V}\right)_T -$, $\left(\frac{\partial\eta}{\partial V}\right)_p = 0$, $\left(\frac{\partial\eta}{\partial V}\right)_T < \left(\frac{\partial\eta}{\partial V}\right)_p$
IV	Intermediate densities	$\left(\frac{\partial\eta}{\partial T}\right)_p -$, $\left(\frac{\partial\eta}{\partial T}\right)_V +$, $\left(\frac{\partial\eta}{\partial T}\right)_p < \left(\frac{\partial\eta}{\partial T}\right)_V$	$\left(\frac{\partial\eta}{\partial p}\right)_T +$, $\left(\frac{\partial\eta}{\partial p}\right)_V +$, $\left(\frac{\partial\eta}{\partial p}\right)_T > \left(\frac{\partial\eta}{\partial p}\right)_V$	$\left(\frac{\partial\eta}{\partial V}\right)_T -$, $\left(\frac{\partial\eta}{\partial V}\right)_p -$, $\left(\frac{\partial\eta}{\partial V}\right)_T < \left(\frac{\partial\eta}{\partial V}\right)_p$
V		$\left(\frac{\partial\eta}{\partial T}\right)_p -$, $\left(\frac{\partial\eta}{\partial T}\right)_V = 0$, $\left(\frac{\partial\eta}{\partial T}\right)_p < \left(\frac{\partial\eta}{\partial T}\right)_V$	$\left(\frac{\partial\eta}{\partial p}\right)_T +$, $\left(\frac{\partial\eta}{\partial p}\right)_V = 0$, $\left(\frac{\partial\eta}{\partial p}\right)_T > \left(\frac{\partial\eta}{\partial p}\right)_V$	$\left(\frac{\partial\eta}{\partial V}\right)_T -$, $\left(\frac{\partial\eta}{\partial V}\right)_p -$, $\left(\frac{\partial\eta}{\partial V}\right)_T = \left(\frac{\partial\eta}{\partial V}\right)_p$
VI	Liquids under most conditions (see Fig. 2)	$\left(\frac{\partial\eta}{\partial T}\right)_p -$, $\left(\frac{\partial\eta}{\partial T}\right)_V -$, $\left(\frac{\partial\eta}{\partial T}\right)_p < \left(\frac{\partial\eta}{\partial T}\right)_V$	$\left(\frac{\partial\eta}{\partial p}\right)_T +$, $\left(\frac{\partial\eta}{\partial p}\right)_V -$, $\left(\frac{\partial\eta}{\partial p}\right)_T > \left(\frac{\partial\eta}{\partial p}\right)_V$	$\left(\frac{\partial\eta}{\partial V}\right)_T -$, $\left(\frac{\partial\eta}{\partial V}\right)_p -$, $\left(\frac{\partial\eta}{\partial V}\right)_T > \left(\frac{\partial\eta}{\partial V}\right)_p$

Under ordinary conditions there is no continuous gradation of densities available, and so it is in the critical region where such intermediate densities do exist that the change of sign must be sought. The most important point to be decided is whether or not $(\partial\eta/\partial T)_V$ and $(\partial\eta/\partial T)_p$ become zero under the same conditions. The last paragraph pointed out the approximate location of the change of sign for $(\partial\eta/\partial T)_V$. Inspection of Table I compiled from Stakelbeck's data on the viscosity of carbon dioxide shows that $(\partial\eta/\partial T)_p$ is zero along a locus 10 or 15 atmospheres less than the condensation pressure. The zig-zag line in the table is drawn between the pressures where the vapor pressures lie, i.e., it is the condensation line. Furthermore comparison of Table I with Table II taken from Amagat[6] shows that in the liquid region below the condensation line $(\partial\eta/\partial T)_V$ is positive and not negative as it is for liquids under ordinary conditions i.e. farther removed from the critical point. These data show that on the basis of the sign and relative magnitude of the two viscosity temperature coefficients a given state of a fluid can be placed in one of six categories, or loci, as shown in the first three columns of Table III.

In Table I Stakelbeck's data have been

[6] Amagat, Ann. chim. phys. [6] **29**, 68 (1893).

changed from kg sec. per meter^2 and kg per cm^2 to millipoises and atmospheres in order to compare with Phillips'[7] earlier, but less extensive measurements in the same region. The excellence of the agreement between these two investigators gives justification for basing such important conclusions on Stakelbeck's data. Phillips' data on the volumes of carbon dioxide also agree very well with those of Amagat.

In the further development we shall use the general mathematical equations relating four variables any two of which may be taken as independent:

$$(\partial\eta/\partial p)_V=(\partial\eta/\partial p)_T+(\partial\eta/\partial T)_p(\partial T/\partial p)_V, \quad (1)$$

$$(\partial\eta/\partial T)_V=(\partial\eta/\partial T)_p+(\partial\eta/\partial p)_T(\partial p/\partial T)_V, \quad (2)$$

$$(\partial\eta/\partial T)_p=(\partial\eta/\partial T)_V+(\partial\eta/\partial V)_T(\partial V/\partial T)_p, \quad (3)$$

$$(\partial\eta/\partial V)_p=(\partial\eta/\partial V)_T+(\partial\eta/\partial T)_V(\partial T/\partial V)_p, \quad (4)$$

$$(\partial\eta/\partial p)_T=(\partial\eta/\partial p)_V+(\partial\eta/\partial V)_p(\partial V/\partial p)_T, \quad (5)$$

$$(\partial\eta/\partial V)_T=(\partial\eta/\partial V)_p+(\partial\eta/\partial p)_V(\partial p/\partial V)_T, \quad (6)$$

$$(\partial\eta/\partial V)_T=(\partial\eta/\partial p)_T(\partial p/\partial V)_T, \quad (7)$$

$$(\partial\eta/\partial V)_p=(\partial\eta/\partial T)_p(\partial T/\partial V)_p, \quad (8)$$

$$(\partial\eta/\partial p)_V=(\partial\eta/\partial T)_V(\partial T/\partial p)_V, \quad (9)$$

where $(\partial V/\partial T)_p$, $(\partial T/\partial p)_V$, $(\partial T/\partial V)_p$ and $(\partial p/\partial T)_V$ are all positive, and $(\partial V/\partial p)_T$ and $(\partial p/\partial V)_T$ are both negative.

It is well known from kinetic theory that $(\partial\eta/\partial p)_T$ is zero and that $(\partial\eta/\partial p)_V$ is positive for dilute gases. Also it is well known from experiment that $(\partial\eta/\partial p)_T$ is positive for ordinary liquids. From Eq. (9) $(\partial\eta/\partial p)_V$ is negative for ordinary liquids, since $(\partial\eta/\partial T)_V$ is negative and $(\partial T/\partial p)_V$ is positive. It is obvious therefore that $(\partial\eta/\partial p)_T$ must increase from zero as the volume decreases, and that $(\partial\eta/\partial p)_V$ must decrease as the volume decreases, becoming equal to $(\partial\eta/\partial p)_T$ and equal to zero at intermediate densities. Eq. (1) shows that $(\partial\eta/\partial p)_V=(\partial\eta/\partial p)_T$, when $(\partial\eta/\partial T)_p=0$ (locus III). Eq. (9) shows that $(\partial\eta/\partial p)_V=0$, when $(\partial\eta/\partial T)_V=0$ (locus V).

From Eqs. (7) and (8), respectively, it is seen that $(\partial\eta/\partial V)_T=0$ and $(\partial\eta/\partial V)_p$ is positive for dilute gases. The same relations show that both coefficients are negative for ordinary liquids.

[7] Phillips, Proc. Roy. Soc. **87A**, 48 (1912).

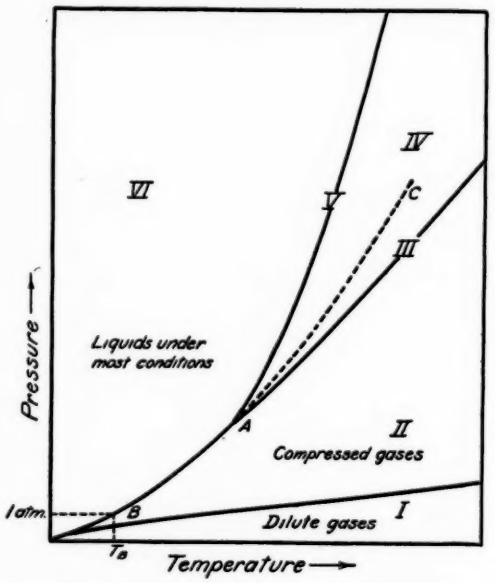

FIG. 2. Schematic "phase diagram" for viscosity. The Roman numerals designate the viscosity loci as defined in Table III. B is the normal boiling point, C is the critical point, and BAC is the vapor pressure curve. Locus IV extends on both sides of AC.

From Eq. (5) it is seen that $(\partial\eta/\partial V)_p=0$, when $(\partial\eta/\partial p)_V=(\partial\eta/\partial p)_T$ (locus III). From either Eq. (4) or (6) it is seen that $(\partial\eta/\partial V)_T=(\partial\eta/\partial V)_p$ when $(\partial\eta/\partial p)_V$ and $(\partial\eta/\partial T)_V$ are zero (locus V). The last two paragraphs enable us to complete the construction of Table III.

The relations thus deduced for locus IV may be confirmed by referring to Tables I and II, for example that $(\partial\eta/\partial T)_V$ and $(\partial\eta/\partial p)_V$ are both positive instead of negative as for liquids in locus VI. All of Stakelbeck's data for liquid carbon dioxide are in locus IV, but at higher pressures or at lower temperatures carbon dioxide would undoubtedly show the behavior of locus VI.

Fig. 2 shows schematically the approximate location of the six loci for a normal liquid. Locus III and locus V are univariant loci, i.e., they are fixed by specifying one external variable. In an exact sense locus I may also be such a unique locus, located at zero pressure (neglecting slippage, of course). Most measurements of the viscosity of gases have been made at moderate pressures and hence always in loci I and II, and most measurements on liquids have been made at temperatures below the normal boiling point

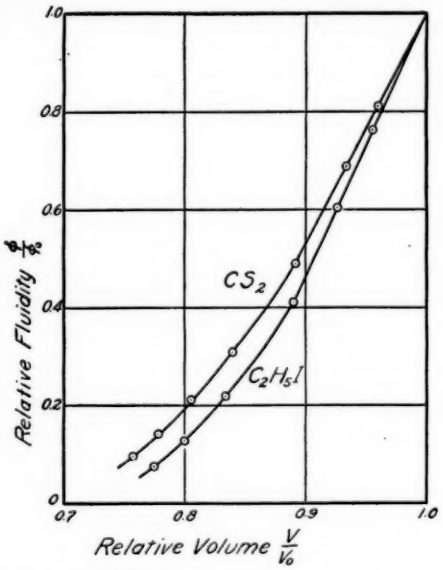

FIG. 3. Relative fluidity relative volume isotherms at 30° for two representative normal liquids, CS_2 and C_2H_5I.

and hence in locus VI. It is notable that locus IV occupies a range of intermediate densities that includes both liquid and gas phases adjacent to the condensation line. The exact location of the boundary curves for any particular substance would require a knowledge of the viscosity over a range of temperatures and pressures from the normal boiling point and one atmosphere up to the critical temperature and pressure.

Bridgman's[2] data show that the viscosity increases with pressure at an increasingly rapid rate, so that at high densities $(\partial\eta/\partial p)_T$ is very large, in fact it appears as though it would approach infinity at extremely high pressures (although freezing would undoubtedly occur first). At very high pressures where $(\partial\eta/\partial p)_T$ is a very large positive number, the other coefficient at constant temperature and the two coefficients at constant pressure become very large negative numbers, as follows:

(1) From Eq. (7) it is seen that $(\partial\eta/\partial V)_T$ becomes very large when $(\partial\eta/\partial p)_T$ is very large.

(2) From Eq. (4) it is seen that $(\partial\eta/\partial V)_p$ is always numerically larger than $(\partial\eta/\partial V)_T$ in locus VI, but the difference becomes small at very high densities since the term $(\partial\eta/\partial T)_V \times (\partial T/\partial V)_p$ does not change greatly with density.

(3) From Eq. (8) it is seen that $(\partial\eta/\partial T)_p$ becomes very large when $(\partial\eta/\partial V)_p$ is very large. However, the two coefficients at constant volume, $(\partial\eta/\partial T)_V$ and $(\partial\eta/\partial p)_V$ remain relatively small numbers even at very high densities as shown by Eqs. (1), (2), (3) and (5).

THE FLUIDITY COEFFICIENTS

Fluidity, defined as the reciprocal of the viscosity, is represented by ϕ. Since $d\phi = -d\eta/\eta^2$ all the relations in Table III are the same for the fluidity coefficients only with all signs reversed, and all inequalities reversed.

The volume coefficients of fluidity of liquids are of particular interest since the constant B in Batchinski's[8] relation

$$\phi = A + BV \tag{10}$$

is a fluidity volume coefficient. Batchinski tested this equation with Thorpe and Rodger's[9] viscosity temperature data for 47 liquids and density temperature data by Thorpe, Young and others, all at atmospheric pressure. All the normal liquids gave straight lines when plotted ϕ *vs.* V. This test showed that fluidity and volume are related linearly as both properties vary with the temperature at constant pressure, i.e., it was a test of the equation

$$\phi(T) = A + BV(T) \tag{11}$$

and $(\partial\phi/\partial V)_p$ is a constant. The volume range tested was that between 0°C and the normal boiling point, approximately a 10 percent change, for the 47 liquids of Thorpe and Rodger, and to temperature above the normal boiling point for benzene, ethyl acetate and ether from the data of Heydweiller.[10] Batchinski did not make this precise a statement of his relation, in fact he tacitly assumed that the fluidity is a linear function of the volume as both properties are varied by varying either temperature or pressure or both simultaneously, i.e., that

$$\phi(p, T) = A + BV(p, T). \tag{12}$$

This statement of the relation implies that the fluidity is a function of the volume only, and

[8] Batchinski, Zeits. f. physik. Chemie **84**, 643 (1913). This relation can be put into several forms. In the form used here V is the molal volume, and A and B are constants.

[9] Thorpe and Rodger, Trans. Roy. Soc. (London) **185A**, 307 (1894).

[10] Heydweiller, Ann. d. Physik **59**, 193 (1896).

TABLE IV. *Fluidity volume coefficients of liquids.*

Liquid	$(\partial\phi/\partial V)_p$ at 1 atmos.	$(\partial\phi/\partial V)_T$ at 30°
CS_2	28.0	22.9[1]
CCl_4	13.7	10.8
Ether	23.6	23.0[1]
C_2H_5Br	23.0	17.3
C_2H_5I	18.4	11.9
n-C_5H_{12}	22.5	17.0
n-C_6H_{14}	18.0	14.4
n-C_8H_{18}	13.2	9.1
C_6H_6	22.05	14.2
C_6H_5Cl	—	12.5
C_6H_5Cl	—	9.4
Acetone	28.7	24.7

[1] Faust's data give for CS_2, 23.6 at 20° and 19.8 at 40°, and for ether, 21.1 at 20° and 19.4 at 34°.

that $(\partial\phi/\partial p)_V$ and $(\partial\phi/\partial T)_V$ are both zero. This is not true as we have seen, for both these coefficients are small positive numbers for liquids in locus VI. Eq. (12) is therefore not true.

Batchinski has tested Eq. (11). The analogous relation

$$\phi(p)=A'+B'V(p) \qquad (13)$$

has never been tested. The only data available for such a test are those of Bridgman[2] and Faust,[5] neither of which were available at the time of Batchinski's paper. These viscosity data under pressure and also the volume data (from Bridgman and Amagat) are not nearly as accurate as the data at atmospheric pressure used by Batchinski to test Eq. (11). Making allowances for these possible inaccuracies the relation appears to be true for all normal liquids tested. Fig. 3 shows a plot of $\phi/\phi_0(p)$ *vs.* $V/V_0(p)$ for two representative liquids, carbon disulfide and ethyl iodide, at 30° from Bridgman's data (ϕ_0 and V_0 are the fluidity and molal volume at atmospheric pressure). It is seen that $(\partial\phi/\partial V)_T$ is constant over a limited volume change, up to about 10 percent. The numerical value of $(\partial\phi/\partial V)_T$ is gotten by multiplying the slope of the curve at any point by ϕ_0/V_0, which for the linear part of the curve gives 22.9 for CS_2 and 11.9 for C_2H_5I.

According to Table III, $(\partial\phi/\partial V)_p$ should be greater than $(\partial\phi/\partial V)_T$ in locus VI. Table IV gives $(\partial\phi/\partial V)_p$ at atmospheric pressure in the temperature range between 0°C and the normal boiling point taken from Thorpe and Rodger's data, and $(\partial\phi/\partial V)_T$ at 30° in the pressure range from 1 to 500 kg/sq. cm calculated from Bridgman's data. V is the molal volume in both cases. It is seen that $(\partial\phi/\partial V)_T$ is about 2/3 to 3/4 of $(\partial\phi/\partial V)_p$ in most cases.

A Study of the Liquid State

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A theory of holes in liquids is developed to account for the thermal and mechanical properties of the liquid state. The treatment is founded on the assumption that the thermal motion of the liquid is determined by the motion of its "surface," this surface, however, to be understood in a broader sense so as to include internal boundaries of which the liquid forms as many as its number of degrees of freedom will permit. An equation of state is obtained and applied to liquid argon, and very close agreement with the empirical data is reached.

AS Bauer, Magat and Surdin[1] have recently demonstrated, various properties of a large number of pure liquids, most strikingly perhaps their molecular volumes, can be brought into correspondence with each other when plotted on a reduced temperature scale with the triple point as zero and the critical point as unity. This suggests a simple mechanism common to pure liquids and adds new emphasis to our lack of a picture in terms of which the mechanical and thermal properties of the liquid state could be understood in as general, if idealized, a manner as we understand the rarefied gases and solid bodies. At the same time, to be accessible from the mathematical side, such a picture ought to provide some information about approximately normal modes of motion of a liquid in the same sense as the positional coordinates and momenta of gas molecules, or the amplitudes and frequencies of elastic waves in a solid, are descriptive of normal modes of motion of their respective phases. But, of course, it remains questionable whether a simple and equally convincing description of the liquid state can be given.

Here it is proposed to describe the motion of a liquid by means of a new set of variables for which the assumption seems reasonable that cross terms in the potential and the kinetic energy vanish. It is assumed that all $3N$ degrees of freedom which one mole of monatomic liquid has are divided into a large number of small groups, each group operative in maintaining a spherical cavity in the liquid, of variable position and size. A cavity, or hole, is not accessible to the center of a molecule except at the expense of heat of evaporation, which is available only in a very few cases. It is further assumed that the liquid surrounds the holes as if it were an incompressible fluid[2] of volume V_0, and that the equations of hydrodynamics are obeyed by the fluid sufficiently well to give the right kinetic energy of a configurational change.

We postulate in other words that the state of motion of the liquid is determined at any moment by the motion of its "surface," this surface, however, to be understood in a broader sense so as to include internal boundaries of which the liquid forms as many as its number of degrees of freedom will permit.

The concept of holes in solids[3] and liquids[4] is not a new one in itself; though it appears that previous authors have restricted their attention to holes of molecular size. In fact, the author's approach to the liquid state has been largely stimulated by Eyring's particularly interesting publication on viscosity. Eyring has stressed the importance of molecular holes "for all phenomena in which a part of the matter in a condensed phase moves with respect to the other parts," obtaining a theory of viscosity and related phenomena in liquids as well as a qualitative understanding of the law of the rectilinear diameter. It should be born in mind, however, that the duality which holes of fixed molecular size bear to molecules in the vapor phase, of necessity fixes their respective numbers to be very nearly equal to each other. If such is truly the case only a very small fraction of the total number of degrees of freedom can be accounted

[1] Bauer, Magat and Surdin, J. de phys. et rad. **7**, 441 (1936).

[2] We shall reserve the word "fluid" for use in this sense, meaning the bulk of matter surrounding the holes.

[3] J. Frenkel, Acta Physicochimica **4**, 567 (1936).

[4] J. Frenkel, Acta Physicochimica **3**, 633, 913 (1935); H. Eyring, J. Chem. Phys. **4**, 283 (1936).

for in terms of holes (about one in a thousand in the lower temperature range). In contrast with this situation the picture given here places the number of holes within the order of magnitude of liquid molecules, and in the extreme case to which the idealization will be carried here accounts for all degrees of freedom. Thus it becomes possible to extend the scope from a mere investigation of structural features to one which aims at a full statistical description of the liquid and treatment as a thermodynamical system.

Tentatively one may wish to identify the numerous holes postulated here with the inhomogeneities in density (or compressibility) which have been postulated by Lucas[5] (to account for the high absorption of supersonic waves in liquids observed by Biquard[6]).

Perhaps it is only proper to point out that the assumptions in the form stated involve a good deal of idealization and, being meant as a first approach from a somewhat unorthodox direction, they must not be taken too literally. In the first place, clearly the whole emphasis is placed on what probably is one feature in a notoriously complex situation. The implication that lattice vibrations, or elastic waves, can be ignored in the liquid is probably not correct at lower temperatures; they may have to be considered as another alternative for disposing of part of the degrees of freedom. In view of the good agreement obtained for the temperature-volume relation on the present assumption one might feel tempted to think that lattice vibrations play a minor role in liquids.

Secondly, in connection with holes of approximately molecular size the notion of a surrounding ideal fluid must be used with very considerable caution. On the other hand, no very specific conclusions from this notion are being used; the result that the effective mass of a hole turns out to be proportional to the amount of liquid displaced may be expected to result from almost any theory, continuous or otherwise.

Thirdly, the conception of surface tension used in this paper will probably have to be adapted more rigorously to the special situation of very small holes. The ground for this has been well prepared by the treatment which surface tension has been given by Born and Courant[7] a long time ago, and can probably be done without change in the fundamental concepts.

Under the Boltzmann principle, spherical boundaries have the obvious advantage of minimum potential energy over other shapes. Consistently with Born and Courant's theory just referred to, each hole must be permitted small vibrations about the ideal sphere, and each vibration contributing through the surface tension σ to the free energy of a hole must be counted as one degree of freedom of that hole. Born and Courant's treatment accounts for the remarkable empirical relation between surface tension and temperature, first announced by Eötvös. We shall make a very explicit use of Eötvös' law but, for the present purpose, shall use a slightly different formulation by L. Brillouin.[8] This author obtains a simpler and yet numerically satisfactory formula by considering capillary surface waves as the carriers of the thermal agitation of the surface molecules.

Thus each hole must be endowed with degrees of freedom of three kinds: One expansional degree q, which measures the radius of the hollow sphere; three translational degrees x, y, z, which describe the position of its center; and a variable number f of vibrational degrees, connected with surface vibrations. The number of the latter is proportional to the area. As the holes grow bigger with rising temperature, degrees of freedom of still another kind will enter into consideration because a small number of molecules evaporate into the bigger holes and—having escaped from the zone of influence of their neighbors—behave much like vapor molecules, i.e., as mass points with three independent degrees of freedom each. Later it will be explained how a number of circumstances cooperate in effectively reducing the frequency with which this process occurs so that it can be treated as a small correction.

1. The Distribution Function

We are concerned with the statistical equilibrium of a system capable of dividing its $3N$

[5] R. Lucas, Comptes rendus **201**, 1171 (1935). See also: Trans. Faraday Soc. **33**, 130 (1937).
[6] P. Biquard, Thesis, Paris. Comptes rendus **202**, 117 (1936).
[7] Born and Courant, Physik. Zeits. **14**, 731 (1913).
[8] L. Brillouin, Comptes rendus **180**, 1248 (1925).

degrees of freedom into $n=\sum_i n_i$ groups of (f_i+4) each, in such manner as to render the total entropy S a maximum. Defining the "molal" surface a_m

$$a_m = N^{\frac{1}{3}} V^{\frac{2}{3}} \tag{1}$$

as the area of a surface layer of N molecules, and therefore with $3N$ degrees of freedom,[8] we have for the total number of degrees of freedom of a mole of liquid:

$$\begin{aligned} 3N &= \sum n_i(f_i+4) = 4n + (3N/a_m)\sum a_i n_i \\ &= 4n + 3a(N/V)^{\frac{1}{3}} \end{aligned} \tag{2}$$

where $a=\sum a_i \cdot n_i$. The subscripts i refer to holes of a particular size q_i, and the summation goes from zero to infinite size. The subscript notation will be dropped as the sums are later replaced by integrals. If we denote the entropy per unit surface area by s_a, we have the extremal condition for S at constant volume V and energy $E=\sum n_i E_i$:

$$\begin{aligned} 0 &= (1/k)\delta S \equiv \delta[n \ln n - \textstyle\sum n_i \ln n_i + a(s_a/k)] \\ &= \delta n(\ln n + 1) - \textstyle\sum \delta n_i(\ln n_i + 1) + \delta a(s_a/k) \end{aligned} \tag{3}$$

subject to the conditions that:

$$\delta n - \textstyle\sum \delta n_i = 0, \tag{4}$$

$$\delta a - 4\pi \textstyle\sum q_i^2 \delta n_i = 0, \tag{5}$$

$$\textstyle\sum E_i \delta n_i = 0, \tag{6}$$

$$(4\pi/3)\textstyle\sum q_i^3 \delta n_i = 0, \tag{7}$$

$$\delta n + \tfrac{3}{4}(N/V)^{\frac{1}{3}}\delta a = 0. \tag{2a}$$

Multiplying (4) to (7) and (2a) with the arbitrary multipliers $(\ln A - 1)$, B, $-1/kT$, $-P/kT$ and C, respectively, and adding to (3) we obtain:

$$\delta n[\ln nA + C] + \delta a\left[B + \frac{s_a}{k} + \frac{3}{4}\left(\frac{N}{V}\right)^{\frac{1}{3}} C\right]$$

$$+ \sum_i \delta n_i\left[-\ln n_i A - 4\pi q_i^2 B - \frac{E_i}{kT} - \frac{4\pi q_i^3}{3kT} P\right] = 0$$

and consequently

$$C = -\ln nA,$$

$$B = -(1/k)s_a + \tfrac{3}{4}(N/V)^{\frac{1}{3}} \ln nA,$$

$$n_i = \frac{1}{A} \exp\{4\pi q_i^2((1/k)s_a - \tfrac{3}{4}(N/V)^{\frac{1}{3}} \ln nA) - (E_i/kT) - (4\pi/3kT)q_i^3 P\}. \tag{8}$$

From the last equation one finds A by summing over n_i and solving. As is seen from (8), A makes its appearance both outside the exponential function and in the exponent. To avoid the complication arising from this we content ourselves with the approximation of calculating the total surface area of all holes, a, from the relation $a=\sum n_i a_i$ as if the total number of holes were known, striking at the same time C from our list of multipliers. With a determined as a function of n, we can then proceed to find n from Eq. (2). We thus get:

$$n_i = \frac{1}{A} \exp -1/kT[E_i - 4\pi q_i^2 s_a T + (4\pi/3)q_i^3 P],$$

$$A = \frac{1}{n}\int_0^\infty dq \iiint_V dx dy dz \int_{-\infty}^{+\infty}\int\int\int dp dp_x dp_y dp_z$$

$$\times \exp -1/kT[E_i - 4\pi q^2 s_a T + (4\pi/3)q^3 P]. \tag{9}$$

To carry out the integration we must express E_i as the sum of potential energy necessary to form a hole, and its kinetic energy of translation and expansion:

$$E_i = 4\pi\sigma_0 q_i^2 + k_i(p, p_x p_y p_z). \tag{10}$$

To find the kinetic energy of translation we use the well-known theorem of classical hydrodynamics stating that the apparent mass of a sphere moving in a frictionless liquid is increased by one-half of the mass of liquid displaced. Thus the apparent mass of translation, and the kinetic energy going with it, are given by:

$$m_i = (2\pi\mu/3)q_i^3, \quad k_{xyz} = (\pi\mu/3)q_i^3(\dot{x}^2 + \dot{y}^2 + \dot{z}^2),$$

where μ is the density of the liquid. Similarly, the apparent mass which a hole exhibits while expanding or contracting, can be found by a simple deduction to be three times the mass of liquid displaced. We consider the kinetic energy of the liquid while receding from the hole at its surface at the rate $\dot{q}$, and at all larger distances at such rate as to maintain a constant density everywhere, flowing away radially. An integration over the infinitely extended liquid gives for the kinetic energy of expansion:

$$k_q = \frac{\mu}{2}\int_q^\infty dr 4\pi r^2\left(\dot{q}\frac{q^2}{r^2}\right)^2 = 2\pi\mu q^3 \dot{q}^2.$$

The kinetic part of (10) is next expressed in terms of the conjugate momenta:

$$k=\frac{\pi\mu q^3}{3}(\dot{x}^2+\dot{y}^2+\dot{z}^2+6\dot{q}^2)$$

$$=\frac{3}{4\pi\mu q^3}(p_x^2+p_y^2+p_z^2+\tfrac{1}{6}p^2). \quad (11)$$

The surface energy can be separated into the free energy $4\pi q^2\sigma$ and an entropy term which cancels against another term in the exponent of (9). Thus the distribution law assumes the form:

$$A\,dn=dq\,dx\,dy\,dz\,dp_x\,dp_y\,dp_z\,dp$$

$$\times\exp-(3/4\pi\mu q^3kT)(p_x^2+p_y^2+p_z^2+\tfrac{1}{6}p^2)$$

$$-1/kT(4\pi\sigma q^2+(4\pi/3)Pq^3), \quad (12)$$

where

$$A=\frac{1}{n}\int_0^\infty dq\int\int\int_V dx\,dy\,dz\int\int\int\int_{-\infty}^{+\infty} dp\,dp_x\,dp_y\,dp_z$$

$$\times\exp-(3/4\pi\mu q^3kT)(p_x^2+p_y^2+p_z^2+\tfrac{1}{6}p^2)$$

$$-1/kT(4\pi\sigma q^2+(4\pi/3)Pq^3)$$

or $$A=\left(\frac{2}{27}\right)^{\frac{1}{2}}(4\pi^2\mu kT)^2\frac{V}{N}\int_0^\infty dq\,q^6$$

$$\times\exp-1/kT(4\pi\sigma q^2+(4\pi/3)Pq^3). \quad (12a)$$

We are now in a position to identify the multiplier P with the external pressure acting on the liquid. Let us consider a hole in a given configuration (x, y, z, q) but with its remaining degrees of freedom in their average distribution. Then its free energy as represented by the expression in brackets in the exponent of (12a) consists of two parts, the first of which accounts exactly for the free surface energy of the hole. The remaining part therefore when differentiated with respect to the volume gives P as the pressure acting on the hole, or on any other hole. Therefore, P must be interpreted as the pressure at the external surface of the liquid.

To find the number n of all holes present at a given temperature T and pressure P, we must first determine the total surface a, and use Eq. (2):

$$a=4\pi\int\ldots\int dq\cdots dp_z n_i q_i^2=4\pi\int\ldots\int dn q^2.$$

This, after introducing a new integration variable

$$x=(4\pi\sigma/kT)^{\frac{1}{2}}q \quad (13)$$

reduces to

$$\frac{a}{n}=4\pi\frac{\left(\frac{kT}{4\pi\sigma}\right)^{9/2}\int_0^\infty dx\,x^8e^{-x^2-\alpha x^3}}{\left(\frac{kT}{4\pi\sigma}\right)^{7/2}\int_0^\infty dx\,x^6e^{-x^2-\alpha x^3}}=\frac{kT}{\sigma}\frac{I_8(\alpha)}{I_6(\alpha)}, \quad (14)$$

where $$I_n(\alpha)\equiv\int_0^\infty dx\,x^ne^{-x^2-\alpha x^3};$$

$$\alpha=\left(\frac{kT}{36\pi\sigma^3}\right)^{\frac{1}{2}}P. \quad (15)$$

For ordinary pressures and at temperatures near the melting point, the numerical values of α are of the order of 10^{-3} per atmosphere or less, and the pressure has little influence on the distribution function and on the values of $I_n(\alpha)$. In the case $\alpha=0$ the expression (14) reduces to

$$a=(7/2)(nkT/\sigma), \quad (14a)$$

and the surface free energy of all holes assumes the simple form $7/2nkT$. But with increasing temperature even quite moderate pressures correspond to values of α of the order of unity and exert a very important effect upon the distribution functions. Introducing the value (14) for a into Eq. (2), we find:

$$n=-\frac{3N}{4}\left(1\Big/1+\frac{3}{4}\left(\frac{I_8(\alpha)}{I_6(\alpha)}\right)\frac{kT}{\sigma}\left(\frac{N}{V}\right)^{\frac{1}{3}}\right). \quad (16)$$

Eq. (16) and all other formulas involving σ assume particularly simple and convenient forms when σ is expressed in terms of the Eötvös formula. Choosing the formulation by Brillouin[8]

$$\sigma=\frac{9}{4}k\left(\frac{N}{V}\right)^{\frac{1}{3}}(T_c-T) \quad (17)$$

we finally obtain the following relation for the

total number of holes:

$$n=\frac{3N}{5}\left(1\Big/1+\frac{1}{3}\frac{T}{T_c-T}\frac{I_8(\alpha)}{I_6(\alpha)}\right) \tag{18}$$

with

$$\alpha=\frac{4}{81\pi^{\frac{1}{2}}}\frac{PV}{NkT}\left(\frac{T}{T_c-T}\right)^{\frac{1}{2}} \tag{19}$$

and T_c denoting the critical temperature.

2. An Equation of State

Eqs. (12), (18) and (19) together with the Eötvös formula represent the formal equipment necessary for the calculation of such observable quantities as total energy, free energy and volume of the system at given temperature and pressure. In this note we shall restrict ourselves to determining the volume as a function of the other two variables of state. As an illustration the molal volume of liquid argon will be calculated over its whole temperature range and under its saturation pressure which covers the pressure range up to 48 atmos.

Proceeding in much the same way as in the calculation of the surface area, we find the volume by an integration of $(4\pi/3)q^3$ over all holes:

$$V-V_0=\sum n_i v_i$$

$$=\frac{4\pi}{3}\int\cdots\int dnq^3=\frac{4\pi n}{3}\left(\frac{kT}{4\pi\sigma}\right)^{\frac{1}{2}}\frac{I_9(\alpha)}{I_6(\alpha)}=nv.$$

Here v represents the average volume per hole and can be written by use of (17):

$$v=\frac{4}{81\pi^{\frac{1}{2}}}\frac{V}{N}\left(\frac{T}{T_c-T}\right)^{\frac{1}{2}}\frac{I_9(\alpha)}{I_6(\alpha)}. \tag{20}$$

From a comparison of (19) and (20) it is found, incidentally, that

$$Pv=kT\alpha(I_9(\alpha)/I_6(\alpha)) \tag{21}$$

or

$$P(V-V_0)=nkT\alpha(I_9(\alpha)/I_6(\alpha)). \tag{22}$$

It must be considered that n and α depend on V implicitly in a complicated way; hence, solving for V is most easily accomplished by a trial method. It follows from Eqs. (18) and (20) that nv/V depends on V only through α in a less important way. Thus writing

$$V-V_0=V_0/(V/nv-1)$$

it is found that:

$$V-V_0=\frac{V_0}{27\pi^{\frac{1}{2}}\frac{I_6(\alpha)}{I_9(\alpha)}\left(\frac{T_c-T}{T}\right)^{\frac{1}{2}}\left[1+\frac{1}{3}\frac{T}{T_c-T}\frac{I_8(\alpha)}{I_6(\alpha)}\right]-1}. \tag{23}$$

This formula was used in the following calculations of the volume of argon. Since the numerical value which one has to insert for α presupposes the knowledge of V which is being calculated, a few slightly different values for α must be tried until the calculated volume agrees with the volume first assumed. Since an increase in α must always result in a decrease of the computed V, one is certain that the true value of V must lie between the one originally assumed and the one obtained from (23).

All computations hinge on the evaluation of integrals of the type $I_n(\alpha)$. The thing that immediately suggests itself is a series expansion in powers of α at $\alpha=0$:

$$I_n(\alpha)=\sum_{k=0}^{\infty}(-1)^k\frac{\alpha^k}{k!}\Gamma\left(\frac{n+1}{2}+\frac{3k}{2}\right). \tag{24}$$

Unfortunately this series is not convergent because the gamma-functions increase faster than the factorials in the denominators (the arguments of the gamma-functions increase in steps of 3/2 whereas the factorials increase in unit steps). At first, the expansion coefficients decrease quite rapidly only to begin increasing again when a certain index k is reached. However, for a limited range of values α the first terms of the series converge toward a definite sum and this semi-convergence makes it possible to use Eq. (24) in the low temperature region where α is of the order of 0.01. In order to cover the whole temperature range it was decided to apply numerical quadrature to the integrals I_n, $(n=6, 7, 8$ and $9)$, for a selected number of suitably distributed values of α. The following

recursion formula can easily be seen to be valid:

$$(n+1)I_n(\alpha)=2I_{n+2}(\alpha)+3\alpha I_{n+3}(\alpha). \quad (25)$$

Thus one of the three, I_9 let us say, could simply be found from I_6 and I_8. But in view of the additional check obtained with little extra labor it was thought best to calculate them all independently.

As has been pointed out before, it is necessary to vary α by small amounts until a self-consistent value V is found from Eq. (23). This can very conveniently be done by means of a Taylor expansion about a suitably chosen α. The first and second derivatives can be calculated by the combined use of

$$(d/d\alpha)I_n=-I_{n+3},$$
$$(d^2/d\alpha^2)I_n=I_{n+6}$$

and continued application of (25), until all derivatives are reduced to expressions in I_7, I_8, I_9. We find:

$$\frac{dI_6}{d\alpha}=-I_9, \quad \frac{dI_7}{d\alpha}=-\frac{1}{3\alpha}[8I_7-2I_9],$$
$$\frac{dI_8}{d\alpha}=\frac{16}{9\alpha^2}I_7-\frac{3}{\alpha}I_8-\frac{4}{9\alpha^2}I_9, \quad (26)$$
$$\frac{dI_9}{d\alpha}=-\frac{32}{27\alpha^3}I_7+\frac{2}{\alpha^2}I_8-\left(\frac{10}{3\alpha}-\frac{8}{27\alpha^3}\right)I_9,$$

$$\frac{d^2I_6}{d\alpha^2}=-\frac{dI_9}{d\alpha}; \quad \frac{d^2I_8}{d\alpha^2}=I_7\left[-\frac{368}{27\alpha^3}+\frac{128}{243\alpha^5}\right]$$
$$+I_8\left[\frac{12}{\alpha^2}-\frac{8}{9\alpha^4}\right]+I_9\left[\frac{44}{9\alpha^3}-\frac{32}{243\alpha^5}\right], \quad (27)$$
$$\frac{d^2I_9}{d\alpha^2}=I_7\left[\frac{128}{9\alpha^4}-\frac{256}{729\alpha^6}\right]+I_8\left[-\frac{50}{3\alpha^3}+\frac{16}{27\alpha^5}\right]$$
$$+I_9\left[\frac{130}{9\alpha^2}-\frac{368}{81\alpha^4}+\frac{64}{729\alpha^6}\right].$$

A few sets of the integrals I_n and their derivatives were computed and are listed in Table I. Thanks to the possibility of computing intermediate points by means of the Taylor expansions this was found amply sufficient to cover all practical needs. It might appear from the table as if a higher accuracy than necessary has been accomplished in the integrations; actually in some cases this accuracy turns out just sufficient for the calculation of the derivatives. For instance when $(d^2/d\alpha^2)I_9(0.100)$ is calculated with the use of (27), one has to form the difference of very big numbers and the result turns out to be about a thousand times smaller than the individual terms contributing to it.

3. Correction for "Internal Vapor Pressure"

When the size of holes becomes sufficiently big so that molecules can evaporate into them, the effective pressure acting on a hole ceases to be equal to the external pressure but is reduced by the back pressure exerted by the molecules inside of holes. Hence, the average number of holes of a given size q is increased just as if an average back pressure, or internal vapor pressure, were exerted in all holes. If molecules were just as free to evaporate into holes as they are to evaporate into outside space the saturation pressure inside a hole would just counter-balance the external pressure, and a liquid under its own saturation pressure would exhibit no change of volume under its own saturation pressure.

Actually there are various reasons why this is not the case. In the first place, the effective free volume which a molecule acquires when evaporating into a big volume which it shares with a great many other molecules is bigger by a factor e than its share if this same volume were equally divided into compartments, with the exclusive use of one compartment for each molecule.[9] Planck, on page 370 f.,[9] points out the difference between the partition functions of the two cases: The transition from the system of N molecules in their respective compartments of size V/N to the other system where the volume V is shared by N molecules, involves division by $N!$. At the same time the volume accessible to each molecule is increased by a factor N. With the use of the Stirling formula, this introduces a factor $(Ve/N)^N$ into the partition function of the vapor, replacing the factor $(V/N)^N$ which one obtains in the case of N separated

[9] Planck, Ann. d. Physik **66**, 365 (1922). See also, K. Herzfeld, *Kinetische Theorie der Wärme*, Eleventh Edition, p. 150.

TABLE I.

	$I_n(\alpha)$				$(d/d\alpha)I_n(\alpha)$			$(\alpha^2/d\alpha^2)I_n(\alpha)$		
α	$n=6$	7	8	9	6	8	9	6	8	9
0.000	3.3233	6.000	11.631	24.000	−24.000	−120.00	−287.88	287.88	1871.2	5040.0
.100	.91565	1.4703	2.5197	4.5709	− 4.5709	− 17.34	− 36.75	36 75	191.0	317.00
.500	.2391	.3027	.4065	.5743	− .5743	− 1.309	− 2.085	2.085	5.877	10.243
1.200	.070643	.073318	.080455	.09268	− .09268	− .1392	− .18007	.18007	.33049	.46668
2.173	.026031	.023123	.021665	.021296						

molecules. This reduces the internal vapor pressure by a factor e^{-1} compared with the saturation pressure observed at that temperature. Besides, the heat of evaporation from the plane external boundary surface is less than that from a strongly concave surface. This is the exact analog of the well-known increase in vapor pressure at the surface of small drops; only that the curvature of our internal boundaries is of the opposite sign, besides being infinitely stronger than the curvature of the drops which usually serve as an illustration of this phenomenon. Except for the reversed sign, however, the thermodynamical argument proceeds in the same way as for small drops.[10] Taking the relation usually derived, but with inverted sign and inserting an e factor, we write:

$$RT \ln (ep/P) = -2\sigma/sq, \tag{28}$$

where p and P are the vapor pressures inside the holes and outside the liquid respectively, s the density of the liquid and q the radius of the hole considered. Multiplying both sides of (28) with d_0, the density of the outside vapor, and invoking the approximate validity of the ideal gas law for the vapor we obtain:

$$P \ln (ep/P) = d_0 RT \ln (ep/P) = -(2\sigma/q)(d_0/s).$$

Here a distinction between α and α_0 becomes necessary. Henceforth we shall denote by α_0 the quantity as defined by (19) which was associated with the external pressure P, and reserve the letter α for a quantity similarly associated with $(P-p)$:

$$\alpha = \alpha_0 - \alpha'; \quad \alpha' = \frac{4}{81\pi^{\frac{1}{2}}} \frac{pV}{NkT} \left(\frac{T}{T_c - T}\right)^{\frac{1}{2}}.$$

Introducing α_0 and the integration parameter x previously used, we can write the equation for the internal pressure p:

$$p = P \exp -(1 + (2\sigma/Pq)(d_0/s)$$
$$= P \exp -(1 + \tfrac{2}{3}(d_0/s)(1/d_0 x)). \tag{29}$$

This reduction of the internal vapor pressure should be clearly distinguished from another fact which we have to discuss, namely, that the volume accessible to a molecule which has evaporated into a hole is not the volume of that hole. Owing to the fact that its own volume occupies a considerable portion of the hole in which it is moving, the center of the molecule is restricted to move within a sphere whose radius is smaller than the radius of the hole by one molecular diameter $2q_0$. Consequently, the internal pressure is taken into consideration by the addition of a term $\alpha'(x-x_0)^3$ to the exponent of $I_n(\alpha_0)$; this term counteracts the other one, $-\alpha_0 x^3$, only within the small volume to which the center of the molecule has access.

$$I_n(\alpha) = \int_0^\infty dx\, x^n \exp -x^2 - \alpha_0 x^3 + \alpha'(x-x_0)^3, \tag{30}$$

where

$$x_0 = 2q_0 \left(\frac{4\pi\sigma}{kT}\right)^{\frac{1}{2}} = 3(\pi)^{\frac{1}{2}} \left(\frac{N}{V}\right)^{\frac{1}{2}} \left(\frac{T_c - T}{R}\right)^{\frac{1}{2}} (2q_0).$$

Expressions of the form (30) must be used as the temperature goes to high values. At the same time the number n of holes must be adjusted for the loss of degrees of freedom resulting from the escape of a small fraction of molecules from the fluid. This correction, though small, becomes quite noticeable within a few degrees of the critical temperature. The number of molecules escaped is found by integration over the product of their density $d(q)$—a function of the diameter of the hole—and their accessible volume; the integration extending over all holes.

[10] W. Thomson, Phil. Mag. **42**, 448 (1881); H. v. Helmholtz, Wied. Ann. **27**, 508 (1886).

A simple way to perform this integration is by means of an average density defined as

$$d_{Av}=\frac{1}{I_9(\alpha)}\int dx\, d(x)(x-x_0)^3x^6e^{-x^2-\alpha x^3} \quad (31)$$

with $d(x)=d_0\exp-(1+\frac{2}{3}(d_0/s)(1/\alpha_0 x))$.

The fractional number of molecules escaped—which is equal to the fractional number n'/n of holes lost in this process—is given by

$$\frac{n'}{n}=\frac{d_{Av}}{s}\frac{V-V_0}{V}. \quad (32)$$

For large values of α_0, formulas (29), (30) and (31) can be approximated by a series expansion of the exponential function. Since this case arises at higher temperatures, and thus for bigger holes where a distinction between x and $(x-x_0)$ becomes less important, we approximate (30) by

$$I_n(\alpha)=\int_0^\infty dx\, x^n \times\exp-x^2-\alpha_0(1-1/e)x^3-\tfrac{2}{3}(d_0/es)x^2, \quad (30')$$

which is easily transformed into

$$I_n(\alpha)=\left(1+\frac{2}{3e}\frac{d_0}{s}\right)^{-(n+1)/2}I_n(\alpha_{eff}) \quad (33)$$

with α_{eff} independent of x:

$$\alpha_{eff}=\alpha_0\left(1-\frac{1}{e}\right)\left(1+\frac{2}{3e}\frac{d_0}{s}\right)^{-\frac{1}{2}}. \quad (34)$$

It is of particular advantage to use the approximation offered by these last formulas—which is increasingly close as the critical temperature is approached—because the numerical values which α_{eff} assumes in the high temperature range are a repetition of those which α_0 assumes at much lower temperatures where no correction for internal back pressure is necessary. Thus we are able to make a two-fold use of every set of integrals I_n listed in Table I, first at that temperature where the particular parameter value α for which it was determined coincides with α_0, and again at the higher temperature where the same value results for α_{eff}.

4. Limiting Values at the Critical Point

While it is too much to expect that our formulas should remain valid right up to the critical point, it is interesting that they remain finite and lead to simple limiting forms as T approaches T_c. This can be demonstrated by expanding $I_n(\alpha_0)$ in inverse powers α_0^{-k}:

$$\int_0^\infty dx\, x^ne^{-x^2-\alpha x^3}=\tfrac{1}{3}\sum_{k=0}^{\infty}(-1)^k\frac{1}{k!\alpha^{\frac{1}{3}(n+2k+1)}}\Gamma\left(\frac{n+2k+1}{3}\right),$$

from which it is immediately seen that

$$\lim_{\alpha\to\infty}\frac{I_9(\alpha)}{I_6(\alpha)}=\frac{7}{3\alpha}$$

and

$$\lim_{\alpha\to\infty}\frac{I_8(\alpha)}{I_6(\alpha)}=\alpha^{-\frac{1}{3}}\frac{\Gamma(9/3)}{\Gamma(7/3)}=\frac{1.679}{\alpha^{\frac{1}{3}}}.$$

The first of these equations furnishes the limiting form of Eq. (21):

$$\lim_{T\to T_c}v=\frac{kT_c}{P_c}\lim_{\alpha\to\infty}\alpha\frac{I_9(\alpha)}{I_6(\alpha)}=\frac{7}{3}\frac{T_c}{P_c}.$$

The second when introduced into (18) gives:

$$\lim_{T\to T_c}n=\frac{3N}{4}\frac{1}{1+\frac{1}{3}\left[\frac{81(\pi)^{\frac{1}{2}}}{4}\frac{NkT_c}{P_cV_c}\right]^{\frac{1}{3}}\lim_{\alpha\to\infty}\left(\alpha^{\frac{1}{3}}\frac{I_8(\alpha)}{I_6(\alpha)}\right)}$$

$$=\frac{3N}{4}\frac{1}{1+1.159\times10^6(T_c/P_cV_c)^{\frac{1}{3}}}.$$

Similarly, applying the correction for back pressure as expressed by Eqs. (33) and (34), we find:

$$\lim_{T\to T_c}v=\frac{7}{3}\frac{e}{e-1}\frac{kT_c}{P_c}, \quad (35)$$

$$\lim_{T\to T_c}n=\frac{3N}{4}\frac{1-n'/n}{1+1.159(e/e-1)(T_c/V_cP_c)^{\frac{1}{3}}\times10^6}. \quad (36)$$

The volume V_c at the critical point is then obtained by forming $(nv)_c$:

$$V-V_0=\frac{7NkT_c}{4P_c}\frac{1-n'/n}{1-1/e+1.159\times10^6(T_c/V_cP_c)^{\frac{1}{3}}}$$

with $$\frac{n'}{n} \sim \frac{1}{e} \frac{V - V_0}{V}.$$

Actually, the volume at the critical point is much larger than the one obtained from our last formula. This disagreement is not surprising since Eötvös' law cannot be expected to hold near the critical temperature at the interface between liquid and vapor; it is derived for the interface between liquid and vacuum.

5. The Volume of Liquid Argon Under its Saturation Pressure

Using the equation of state derived in a preceding section, the volume of one mole of liquid argon has been calculated over the temperature range from the freezing point to the critical temperature; in this temperature range the saturation pressure of the vapor varies from zero to 48 atmos. In different parts of this temperature range Eq. (23) must be used in different

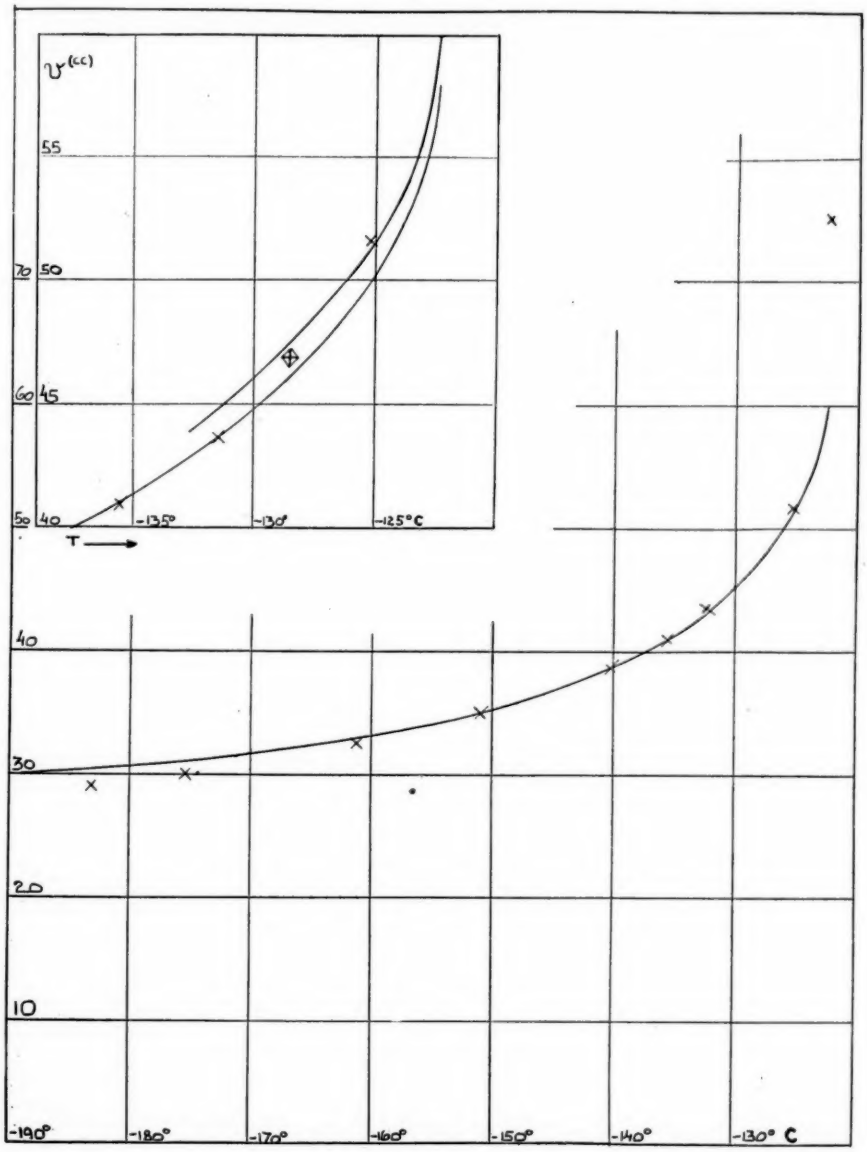

Fig. 1.

ways, in accordance with what has been said in Section 3. It was found that in the lower temperature range up to about 140°K the corrections resulting from internal back pressure can be neglected entirely, and that α can be identified with α_0. For the remaining temperature range the back pressure becomes increasingly important and it was taken into consideration in the approximation represented by (33), (34). To ignore it would result in too small volumes as computed from (23). On the other hand, by considering it in the approximation indicated one is led to slightly too large volumes. In fact, (33) and (34) provide an upper limit rather than the true volumes; these latter being rigorously expressed by formulas (23), (30) and (32). Only for one temperature was the volume computed in the rigorous manner; namely for 144.7°K which lies in the very region where the back pressure is not negligible yet is not big enough to be approximated by formulas (33) and (34).

Results are listed in Table II, and are also summarized in Fig. 1 together with the empirical values (represented by crosses) measured by Mathias, Kamerlingh Onnes and Crommelin.[11] The saturation pressures given in the second column of Table II were taken from the measurements of Crommelin, and of Holst and Hamburger.[12] The values for V as given in the table were computed assigning to V_0 a value of 27.40 cc/mole. The results obtained when neglecting the effect of internal back pressure, as listed under column A in Table II, are plotted in the lower curve of inset of Fig. 1. The upper curve represents the results of column C; this curve provides an upper limit for the final curve which should gradually approach it from below. The point for $T=-128.3$°C, listed as (B) in column A of Table II, is represented in the inset as a little square; it indicates more definitely how the final curve changes gradually from the lower to the upper curve. Interpolating in this manner, the final curve was obtained as drawn in the main diagram of Fig. 1.

TABLE II.

		A: No back pressure			C: Back pressure approximated by (33), (34)		
T°K	$P\,.10^{-7}$	α_0	V/V_0	V	α_{eff}	V/V_0	V
84	.089	$0.5\ 10^{-7}$	1.095	30.000			
100	.325	$9.48\ .10^{-4}$	1.145	31.37			
110	.675	.00299	1.191	32.64			
120	1.16	.0054	1.262	34.60			
125	1.58	.01638	1.308	35.83			
138	2.94	.10753	1.512	41.42			
140.45	3.24				0.1026	1.614	43.8
144.6	3.78	.4805	1.692	46.35			
144.68	3.79	$.5000^B$	1.7113^B	46.89^B			
146.3	4.00				.5092	1.810	49.6
148.0	4.25	2.075	1.82	50.2	1.1764	1.881	51.53

The agreement throughout the range is surprisingly close, considering how little attention has been given in this treatment to the more intimate effects which the discontinuous character of the liquid must exert on the processes we are dealing with. Minor deviations occur near the freezing point where some of our assumptions are most certainly to be replaced by more appropriate ones. This remains an object for further study.

This work was planned, and carried out in part, at the University of Vienna where it was reported at the I. Chemisches Institut in the early part of November 1936. From the latter part of that month the work has been continued at the Frick Chemical Laboratories of Princeton University.

[11] Mathias, Kamerlingh Onnes, Crommelin, Comm. Phys. Lab. Leyden No. 131 a. See also, Landolt-Börnstein, *Physikalische Tabellen*, Vol. I, p. 273.

[12] Crommelin, and Holst and Hamburger. See Landolt-Börnstein II, p. 1332.

A Partition Function for Liquid Mercury

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From a model for liquid mercury we have formulated a partition function of sufficient generality to give by means of the usual statistical mechanical equations the vapor pressure, the equation of state, the entropy of melting and the specific heats. The partition function involves four parameters characterizing the particular substance concerned. Having chosen these parameters for mercury it is possible to calculate all the above properties from the melting point to the boiling point within experimental error except for a slight divergence of about 2 percent (0.1 cal./mole/degree) in the specific heat at the melting point. The van der Waals' constants follow from the theory and when employed in his equation give satisfactory agreement between calculated and observed critical properties. The long liquid range, low melting point, and low viscosity of metals are all in agreement with our model in which it is assumed that in the liquid the kernels move independently of their valence electrons.

INTRODUCTION

WE are here concerned with developing and applying a simple model for liquids which will lead to a partition function sufficiently general for all the thermodynamic properties to be derived from it. We use the conception of a free volume, in which liquid molecules move, developed in earlier papers from this laboratory,[1-3] but suitably modified to take account of the temperature coefficient of the volume available to the molecules. This makes an important addition to the free volume, and is of even greater importance in calculations of the specific heats. We have chosen mercury as our test liquid for two reasons. First because there is adequate experimental data and second because it appeared anomalous in the earlier treatment of Eyring and Hirschfelder.

The partition function derived below may be expected to apply to close-packed monatomic liquids, e.g., many of the liquid metals and perhaps the rare gases near their melting points. The essential postulates may be stated as follows. The total energy (in excess of the zero-point energy) may be divided into two parts: first, the kinetic and potential energy of displacements from the equilibrium positions, and second the potential energy that the liquid would have if the atoms remained static in their mean positions. For lack of better names we will call the first the dynamic and the second the static energy. The static energy is assumed to be a function of volume only, while the dynamic energy is chiefly a function of temperature, but also has volume dependence.

The dynamic energy at sufficiently low temperatures is assumed for simplicity to be that of a simple harmonic vibrator. As the temperature is raised and the liquid expands a flat space of zero potential energy is introduced into the curve, the extent of which is governed by the amount of expansion. This behavior may be seen in Fig. 1. It may be observed that the extent of the flat space in the curve determines the ratio of kinetic to potential energy, and that thus this ratio is unity at low temperatures and increases as the temperature is raised at any particular pressure. Both the characteristic frequency of vibration, and the flat space in the potential curve are functions of pressure of course, but in what follows the variation of the frequency with pressure has been assumed to be sufficiently small to be neglected.

Fusion

Hirschfelder, Stevenson and Eyring[3] have discussed the process of fusion and the entropy of melting from essentially this point of view. On their picture of melting the volume of the liquid at the melting point is just great enough so that if a hole appears in the liquid a molecule in a neighboring position can slip into the hole without appreciable activation energy. That this is not true for the solid is indicated by its high viscosity. Thus a body-centered solid lattice

[1] Roy F. Newton and Henry Eyring, Trans. Faraday Soc. **33**, 73 (1937).
[2] Henry Eyring and J. O. Hirschfelder, J. Phys. Chem. **41**, 249 (1937).
[3] J. O. Hirschfelder, D. P. Stevenson and Henry Eyring (To be submitted).

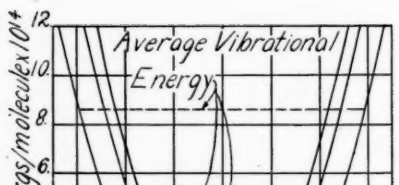

FIG. 1. Potential energy function for displacements from equilibrium position.

composed of incompressible atoms should melt to a liquid of somewhat similar structure having a volume about 20 percent greater than that of the solid at the absolute zero. Since the atoms are compressible, and liquids at the melting point are only quasicrystalline, the observed volume will generally be somewhat smaller than this. The most important term arising in the calculation of the entropy of melting of mercury is the contribution, R, arising from the fact that in the liquid the entire volume is jointly used by the molecules whereas in the solid each molecule is restricted to its own small region in the lattice.

We may think of this mechanism of melting in the following way. Thus we think of a perfect crystal as a single supermolecule whereas the perfect liquid at the melting point results from its complete dissociation. This complete dissociation with its resultant communal sharing of the total free volume among the molecules increases the entropy by R. This we call the communal entropy. This communal entropy of melting of the perfect solid into the perfect liquid may be further modified by volume changes accompanying melting as well as by changes in the rotation of individual molecules. Another not unusual situation is that the process of melting leads to double molecules so that the increase due to communal entropy is only $(\frac{1}{2})R$ with more or less complete compensation of this lowered value arising from the new rotational degrees of freedom of the double molecules. Melting into other types of liquid molecules leads to still other obvious modifications. The breaking of these structures above the melting point provides an explanation for the frequently observed slightly large specific heats we discuss later.

Supercooling, on the other hand, results in the appearance of molecular aggregates which do not readily rearrange into the perfect crystal. Inside the aggregates the communal entropy has been lost, whereas the aggregates themselves still share their free volume and so retain a portion of the communal entropy which, however, gradually disappears with further aggregation. The interior of these aggregates when acted upon by a shearing stress will suffer the characteristic plastic deformation of crystals whereas the aggregates themselves will obey the usual laws of viscous flow and will show the usual high viscosity always associated with large molecules. The energy of activation for viscous flow for the nonmetals is usually about one-third the heat of vaporization.[4] Since any rate process always proceeds simultaneously by all possible mechanisms and therefore principally by the faster ones we expect a glass to exhibit both entropies and viscosities, which depending on the state of aggregation, take all the intermediate values, between the perfect liquid and the perfect solid.

We now consider the peculiarly low activation energy for viscous flow of metals. Since the activation energy has been related by Hirschfelder, Stevenson and Eyring[3] to a hole approximately one-third the size of the molecule we immediately suspect that the particle which flows must be smaller than the atom which vaporizes. This seems highly reasonable from several points of view. First, since the high electrical conductivity of metals indicates that the conducting electrons can flow without the atomic kernels it seems clear that the kernels can undergo the slight displacements necessary to provide the small holes for viscous flow or diffusion without disturbing the electrons. Secondly, since the small kernels do the diffusing (into holes when they appear) the liquid will not need to be nearly as expanded at the melting point as if the whole atom moved as a unit. Thus because of the abnormally small expansion of the metals we should expect abnormally low melting points. This will then lead to an abnormally long liquid range since the vapor, being composed not of kernels but of

[4] H. Eyring, J. Chem. Phys. **4**, 283 (1936).

normal atoms, will possess a normal boiling point. Stated more tersely, the abnormally long liquid range for metals is explained if we assume that the kernels melt while the atoms vaporize. This is exemplified by gallium which, although it melts at a temperature just above room temperature has a liquid range of about 2000° whereas the typical nonmetal melting in the same range will in general have a liquid range of 100° or less.

Our model for the metals is thus consistent with the considerations on cohesion presented by Mott and Jones[5] who, "picture these metals as composed of hard spheres (the ions) held together by the Coulomb attraction between the ions and the valence electrons." Simon,[6] Schubin[7] and Mott[8] have considered the problem of conductivity in liquid metals. Mott gives the equation

$$\frac{\sigma_L}{\sigma_S}=\exp\left(-\frac{2}{3}\frac{\Delta S}{R}\right), \tag{1}$$

which agrees with experiment for a number of the metals; σ_L and σ_S are the conductivity of liquid, conductivity of solid, and entropy of melting respectively. Although this relationship has been derived by assuming that the entire change in entropy arises from the greater amplitude of the characteristic frequency of the liquid, we expect an increase in randomness arising from the communal entropy to have a similar effect in that it too provides a larger electronic target area. A model essentially of the type used in this paper seems necessary from the other considerations developed below.

The partition function

We may now formulate the partition function based on the qualitative arguments given above. The partition function for a monatomic molecule may be written as

$$f(T)=\frac{(2\pi mkT)^{\frac{1}{2}}V_f}{h^3}\exp\left(E(V)/RT\right),$$

where $E(V)$ denotes the expression for the static energy as a function of volume, a function to be discussed later, and V_f is the total free volume available to the molecule. Now since we picture the liquid as being composed of vibrating particles which are not necessarily confined to particular lattice positions, V_f is equal to Nv_f, v_f being defined in terms of the potential curve, illustrated in Fig. 1, for displacements of a single molecule from its equilibrium position.

In order to secure the free volume per molecule, v_f, an explicit expression for the magnitude of the space of zero potential energy must be obtained. Following Hirschfelder and Eyring[2] we have

$$2(V/N)^{\frac{1}{3}}-2(V_0/N)^{\frac{1}{3}}$$

where V_0 is the volume of the liquid at some reference temperature and V is its volume at a point where it has expanded somewhat thus, introducing the flat space into the curve shown in Fig. 1. Both V_0 and V are considered at the same pressure. The complete expression for V_f is then

$$V_f=Nv_f=N\left[2\int_0^\infty \exp\left(-1/2fx^2/kT\right)dx+2(V/N)^{\frac{1}{3}}-2(V_0/N)^{\frac{1}{3}}\right]^3, \tag{2}$$

where f is defined by, $\nu=1/2\pi(f/m)^{\frac{1}{2}}$. On carrying out the integration and rearranging, V_f becomes

$$V_f=N\left[\frac{kT/h\nu}{(2\pi mkT)^{\frac{1}{2}}/h}+2(V/N)^{\frac{1}{3}}-2(V_0/N)^{\frac{1}{3}}\right]^3 \tag{3}$$

accordingly,

$$f(T)=N\left[\frac{kT}{h\nu}+\frac{(2\pi mkT)^{\frac{1}{2}}}{h}2\left((V/N)^{\frac{1}{3}}-(V_0/N)^{\frac{1}{3}}\right)\right]^3\exp\left(E(V)/RT\right). \tag{4}$$

[5] Mott and Jones, *Properties of Metals and Alloys* (Oxford Press), p. 144.
[6] Simon, Zeits. f. Physik **27**, 157 (1924).
[7] Schubin, Physik. Zeits. Sowjetunion **5**, 83 (1934).
[8] N. F. Mott, Proc. Roy. Soc. **A146**, 465 (1934).

We are now in a position to discuss the entropy of fusion, and the closely allied subjects, the specific heats at constant volume and pressure, C_V and C_P. We have for the liquid

$$S-S_0=k[\ln (f(T)/N)^N+N]+\bar{E}/T \tag{5}$$

and for the solid

$$S-S_0=k \ln \kappa(T)+\bar{E}_S/T, \tag{6}$$

where $\kappa(T)$ is defined by

$$\kappa(T)=(kT/h\nu_S)^{3N} \exp (E_S(V)/kT) \tag{7}$$

and

$$\bar{E}=NkT^2(d/dT) \ln f(T), \tag{8}$$

$$\bar{E}_S=kT^2(d/dT) \ln \kappa(T). \tag{9}$$

Then if we define the characteristic temperature, Θ, in the usual way,

$$\Theta=h\nu/k \tag{10}$$

we have

$$\Delta S_f=-1/2R+3R \ln \left[\frac{\Theta_S}{\Theta_l}+2\left(\frac{2\pi mk}{h^2T}\right)^{\frac{1}{2}} \frac{\Theta_S}{(N)^{\frac{1}{3}}}(V^{\frac{1}{3}}-V_0^{\frac{1}{3}})\right] +3RT\frac{1+4/3(1/N)^{\frac{1}{3}}((2\pi mkT)/h^2)^{\frac{1}{2}}\Theta_l(\alpha_l V^{\frac{1}{3}}-\alpha_S V_S^{\frac{1}{3}})}{2T+4((2\pi mkT)/h^2)^{\frac{1}{2}}\Theta_l(1/N)^{\frac{1}{3}}(V^{\frac{1}{3}}-V_0^{\frac{1}{3}})}, \tag{11}$$

where $\alpha \equiv (1/V)(\partial V/\partial T)_P$.

Of the many methods of securing characteristic temperatures for solids Debye's specific heat formula provides the most consistent values. It is justifiable to use Debye's characteristic temperature in the classical vibrational partition function given above since his partition function reduces to the classical form at temperatures high compared to Θ. Since for mercury, Tm is 234°K while Θ is only 84°K, the value of Debye's Θ chosen so as to give the correct thermodynamic properties for the solid at the melting point is the proper quantity to use in the classical vibrational partition function.

Given the value for the characteristic temperature for the solid at the melting point several alternative methods are open for the computation of entropies of fusion. Since we wish to find as nearly the correct model as possible these will be inspected and the one most consistent with experiment will be chosen as most nearly representing the true state of affairs. Hirschfelder, Stevenson and Eyring[3] have taken Θ_l equal to Θ_S and V_0 equal to the volume of the solid at the melting point. Calculations for the monatomic metals where the data were available gave values for ΔS_f consistently too high by about half an entropy unit. The model may be changed to take care of this discrepancy in a number of ways. A better approximation to the dynamic energy function might be secured by allowing the characteristic temperature for the liquid to be an adjustable parameter to be fixed by the entropy of fusion. Thus they found that if Θ_l were taken as 1.1 Θ_S excellent agreement was obtained for the metals considered. Agreement might also be secured by taking $\Theta_l=\Theta_S$ and making V_0 a parameter. Finally V_0 might be taken equal to the volume of the liquid at the melting point, the necessary flexibility being secured by again making Θ_l adjustable. A decision between these alternatives was made by considering the specific heat at constant volume at the melting point. The observed value is 6.06 cal./mole/degree. The first alternative gives 5.39, the second 5.56, and the third $3R$ or 5.96 cal./mole/degree. Obviously, only the last mechanism can be consistent with both the entropy of fusion and the specific heat. It should be noted that it is also the most consistent with our picture of the melting process since we have assumed a quasicrystalline structure for the liquid at the melting point. The value for Θ_l of 79 as compared to 84 for the solid gives the experimental entropy of fusion of 2.38 E.U.[9] A decrease in Θ on going from solid to liquid is

[9] K. K. Kelley, Bulletin 393, Bur. Mines, 1936.

also more reasonable than an increase since one would expect the vibrations in the liquid to be less stiff than those in the solid.

Specific heats

An independent check of the assumptions we have made is afforded by the variation of the specific heats with temperature. C_V is given by—

$$C_V=\left(\frac{\partial E}{\partial T}\right)_V=3R\frac{[T^{\frac{1}{4}}/\Theta+\frac{1}{2}\,1.9281(V^{\frac{1}{3}}-V_0^{\frac{1}{3}})]}{[T^{\frac{1}{4}}/\Theta+1.9281(V^{\frac{1}{3}}-V_0^{\frac{1}{3}})]^2}+\frac{3}{8}\frac{R[T^{\frac{1}{4}}/\Theta\,1.9281(V^{\frac{1}{3}}-V_0^{\frac{1}{3}})]}{[T^{\frac{1}{4}}/\Theta+1.9281(V^{\frac{1}{3}}-V_0^{\frac{1}{3}})]^{\frac{1}{2}}}, \quad (12)$$

where $2(2\pi mk)^{\frac{1}{2}}/hN^{5/6}$ has been replaced by its numerical value of 1.9281. C_p was secured from the thermodynamic formula:

$$C_p=C_V+(T\alpha^2V)/\beta, \quad (13)$$

where values of β, defined by $-(1/V)(\partial V/\partial P)_T$, were secured as outlined below and α was evaluated from the equation given in the *International Critical Tables*. C_P rather than C_V was selected for direct comparison with experiment because the β values for temperatures above room temperature used in formula (13) were evaluated with the aid of the theory outlined below. It is believed, however, that the error introduced in the computation of the term, $T\alpha^2V/\beta$, is quite small. The calculated results are compared with experiment in Table I and in Fig. 2. It may be noted that the minimum in the calcualted curve comes at just the same place as that in the observed one.

The agreement is all that could be expected, the region near the melting point being the only one where the discrepancy is definitely greater than the experimental error. That fact in itself is of some interest. It will be recalled that the observed value for C_V of the liquid at the melting point was 6.06. Now $3R(=5.96)$ is the highest value that can be secured by using simple harmonic potential curves. Since it is not likely that 0.10 cal./mole/degree is contributed to C_V by electronic terms the discrepancy must be due to a more complicated structure in the liquid than the homogeneous form we have assumed for it here. Any association of the liquid will change with temperature in such a way as to absorb more heat near the melting point than the simple structure assumed. This effect has been considered by Simon,[10] by Bernal[11] and by Hirschfelder, Stevenson and Eyring.[3]

TABLE I. *Observed and calculated specific heats.*

$T°$	C_V (calc.)	C_P (calc.)	C_P (obs.)
234	5.96	6.69	6.79
273	5.84	6.65	6.72
293	5.78	6.63	6.67
373	5.63	6.62	6.60
473	5.47	6.61	6.60
573	5.36	6.70	6.67
630	5.32	6.76	6.72

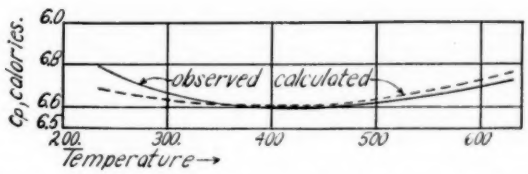

FIG. 2. Calculated and observed molal specific heats of mercury.

It is interesting to note that even though the treatment we are using can be expected to hold best at temperatures below the boiling point the general form of the C_V against T curve is very similar to that given by Bauer, Magot, Surdin[12] for a number of monatomic liquids. Also by taking a reasonable value for the volume at the critical point a value for C_V of about 3.7 is obtained at that temperature. Although the specific heat at constant volume at the critical temperature is not known for mercury this value is in agreement with the values for the few monatomic liquids for which this experimental value is available.

This method gives a means of computing specific heats at constant volume from a knowledge of the entropy of fusion, and the volume of the liquid, the results being, for mercury at least, in excellent agreement with experiment. Specific heats under pressure may also be obtained provided the volume is known. Although the change of C_V with pressure may be obtained thermodynamically a second derivative is necessary, and pressure data are rarely of sufficient accuracy to make this procedure possible. Bridgman[13] has,

[10] Ergebn. exakt. Naturwiss. **9**, 248 (1930); Zeits. f. anorg. allgem. Chemie **203**, 219 (1931).
[11] Trans. Faraday Soc. **33**, 27 (1937).
[12] E. Bauer, M. Magot and M. Surdin, Trans. Faraday Soc. **33**, 81 (1937).
[13] P. W. Bridgman, Proc. Am. Acad. **47**, 347 (1912).

however, estimated C_V for liquid mercury at 0° and 7000 atmos. He finds that over this pressure range C_V increases by 0.121 cal./mole/degree. Substitution of the volumes into Eq. (12) gives 0.114 cal./mole/degree, a value which is probably within the error of the thermodynamic computation.

Compressibilities and vapor pressures

In order to consider compressibilities and vapor pressures a form must be chosen for the function, $E(V)$, giving the static energy of the liquid as a function of volume. Since there is as yet no complete theoretical basis for choosing any particular form, the decision must finally be made on an empirical basis. However, quantum mechanics shows that the repulsive potential terms arising from exchange forces for pairs of molecules fall off exponentially with the distance between the nuclei. Further, Gibson[14] has used an exponential equation to accurately represent the volume of water and aqueous solutions as a function of pressure. Since an exponential term in the equation of state can arise only if such a term occurs in the form for the static energy an expression of the kind $E(V)=f(V)+d\exp(-cV^{\frac{1}{3}})$ is indicated where d and c are constants and $f(V)$ is the attractive part of the static potential. Reasoning again from the case for a pair of molecules the attractive part of the energy, $f(V)$, was assumed to be given by $1/V^m$.

Hildebrand[15] has found that when m is set equal to one the expression gives a good representation of the energy of liquids that are not sufficiently close packed for the repulsive forces to be important. Further it will be recalled that the partition function corresponding to van der Waals' equation is

$$f(T)=(2\pi mkT)^{\frac{1}{2}}/h^3(V-b)\exp(a/VRT), \quad (14)$$

in which the static energy term is of the form a/V. These two considerations, we believe, justify the use of the form a/V for the attractive part of the static energy. A check is provided by the fact that if the considerations given above are valid the numerical value for the constant, a, as determined for the liquid should be essentially the same as that for van der Waals' a. This point will be discussed in detail later. The complete form for $E(V)$ is then:

$$E(V)=a/V-d\exp(-CV^{\frac{1}{3}}) \quad (15)$$

and the partition function becomes

$$f(T)=(2\pi mkT)^{\frac{3}{2}}/h^3N[(kT/h\nu)/(2\pi mkT)^{\frac{1}{2}}/h+2(V/N)^{\frac{1}{3}}-2(V_0/N)^{\frac{1}{3}}]^3\exp(E(V)/RT). \quad (16)$$

The vapor pressure follows from free energy considerations. The free energy of the liquid is given by

$$A(\text{liquid})=kT\ln\frac{[(2\pi mkT)^{\frac{1}{2}}/h^3N((kT/h\nu)/(2\pi mkT)^{\frac{1}{2}}/h+2(V/N)^{\frac{1}{3}}-(V_0/N))^{\frac{1}{3}}]^{3N}}{N^N\exp(-N)}+E(V), \quad (17)$$

while that of the gas is

$$A(\text{gas})=kT\ln\frac{[(2\pi mkT)^{\frac{1}{2}}V_g]^N}{N^N\exp(-N)}. \quad (18)$$

But $$A(\text{gas})-A(\text{liquid})=RT. \quad (19)$$

These relations lead to an explicit expression for the vapor pressure if V_g is replaced by the ideal gas expression, RT/P. We have

$$\frac{1}{P(\text{mm})}=\frac{4.8679}{T}\left[\frac{T^{\frac{1}{2}}}{\Theta}+1.9281(V^{\frac{1}{3}}-V_0^{\frac{1}{3}})\right]^3\times\exp(E(V)/RT). \quad (20)$$

[14] R. E. Gibson, J. Am. Chem. Soc. **56**, 4 (1934).

In assuming mercury vapor to be ideal and monatomic we are not in agreement with some

TABLE II. *Compressibilities and vapor pressures for mercury at atmospheric pressure.*

$T°$	P (calc.)	P (obs.)	β (calc.)	β (obs.)	dV_0/dP
234	2.01×10^{-6} mm	1.99×10^{-6} mm	3.79×10^{-6}		56.0×10^{-6}
273	1.89×10^{-4}	1.88×10^{-4}	4.01	3.93×10^{-6}	56.2
293			4.11	4.08	56.0
373	0.269	0.269	4.54		55.9
473	17.00	17.02	5.09		56.0
573	244.8	245.4	5.72		56.8
630	760.0	760.0	6.13		57.5

[15] J. H. Hildebrand, *Solubility*, second edition (Reinhold Publishing Corporation, 1936).

investigators. Thus, Kelley[16] from free energy considerations concludes that 7 percent of the vapor pressure of mercury at its boiling point is due to diatomic mercury molecules. It should be noted, however, that the vapor pressure calculated from Kelley's free energy data are not consistent with his recommended best values even in the range where no diatomic mercury molecules are supposed to exist. Further, Smith and Menzies[17] have found the density of mercury vapor to be ideal in the range of vapor pressures from one to two atmospheres to within the probable experimental error, about 2 percent.

Two of the three arbitrary constants in $E(V)$ were adjusted to fit the observed vapor pressures, and the third was determined from the compressibilities by a process to be described below. The resulting expression for the static energy in cc atmospheres is

$$E=(11.173\times10^{6})/V \\ -2.346\times10^{13}\exp(-7.80\,V^{\frac{1}{3}}).$$

The observed and calculated values are shown in Table II, the observed values being those recommended by Kelley.[16] The agreement is well within the probable experimental error of the observed values and is unusually good for a two constant equation.

The equation of state is given by the relation

$$P=RT\left(\frac{\partial \ln f(T)}{\partial V}\right)_T \tag{21}$$

and we find

$$PV^{\frac{1}{3}}-\frac{RT\,1.9281[1-(V/V_0)^{\frac{1}{3}}(\partial V_0/\partial P)_T/(\partial V/\partial P)_T]}{T^{\frac{1}{3}}/\Theta+1.9281(V^{\frac{1}{3}}-V_0^{\frac{1}{3}})}+\frac{a}{V^{4/3}}=\frac{cd}{3}\exp(-cV^{\frac{1}{3}}) \tag{22}$$

and if $[1-(V/V_0)^{\frac{1}{3}}(\partial V_0/\partial P)_T/(\partial V/\partial P)_T]$ is considered independent of P,

$$\beta=V^{\frac{1}{3}}\left\{(4/3)\frac{a}{V^{5/3}}-\frac{c^2d}{9}\exp(-cV^{\frac{1}{3}})-\frac{RT(1.9281)^2[1-(V/V_0)^{\frac{1}{3}}(\partial V_0/\partial P)/(\partial V/\partial P)_T]^2}{3[T^{\frac{1}{3}}/\Theta+1.9281(V^{\frac{1}{3}}-V_0^{\frac{1}{3}})]^2}\right\}^{-1}. \tag{23}$$

We have also neglected $(\partial\Theta/\partial P)_T$ since from the behavior of this quantity for the solid we expect it to be small. At low volumes and temperatures, i.e., for the supercooled liquid the term becomes important but since mercury does not form a glass we need not consider this point further at this time.

TABLE III. *Compressions of liquid mercury at 0° and 20°.*

	0°		20°	
P	V (calc.)	V (obs.)	V (calc.)	V (obs.)
1 atmos.	14.755	14.755	14.808	14.808
1,000	14.698	14.698	14.748	14.749
2,000	14.643	14.643	14.689	14.691
3,000	14.588	14.588		
4,000	14.535	14.536	14.579	14.583
5,000	14.485	14.486		
6,000	14.437	14.438	14.479	14.483
7,000	14.392	14.392		
8,000			14.392	14.391
10,000			14.314	14.309

The term, $(\partial V_0/\partial P)_T/(\partial V/\partial P)_T$, arising in Eqs. (22) and (23) merits some discussion. V_0, it will be remembered, is the volume of the liquid at the melting point, and is thus a function of pressure. Since the derivative to obtain the equation of state is taken at constant temperature, the term, $(\partial V_0/\partial V)_T$ which arises is interpreted as being the ratio, $(\partial V_0/\partial P)_T/(\partial V/\partial P)_T$.

Eqs. (22) and (23) were used as follows. For any arbitrary value of the constant, c, the constants a and d were determined from the vapor pressures.[18] Then Eq. (22) was used to determine the value of the term

$$[1-(V/V_0)^{\frac{1}{3}}(\partial V_0/\partial P)_T/(\partial V/\partial P)_T],$$

the value being adjusted so as to give the correct volume at atmospheric pressure. This gave the necessary data for the calculation of volumes under pressure, provided neither Θ nor the term $1-(V/V_0)^{\frac{1}{3}}(\partial V_0/\partial P)_T/(\partial V/\partial P)_T$ were considered

[16] K. K. Kelley, Bull. 383, Bur. of Mines (1935).
[17] A. Smith and A. W. C. Menzies, J. Am. Chem. Soc. 32, 1541 (1910).
[18] Precise vapor pressures are not available over a sufficient range of volumes to make it possible to get accurate values for all three constants from vapor pressure measurements alone.

to be functions of the pressure, an assumption which is probably quite valid for the relatively small pressure ranges considered here. The method of successive approximations may then be used to secure values of a, c and d consistent with both the compressions and vapor pressures.

Since compressions at one temperature serve to fix the value of the parameter, compressions at other temperature, will serve as an independent check. Bridgman[13] has determined volumes of mercury under pressure at 0° and at 20°. The agreement of the calculated values with his observed ones is shown in Table III. Such small discrepancies as exist are probably within experimental error.

A further test of the theory is provided by calculating values for β as a function of temperature. Again the term

$$[1-(V/V_0)^{\frac{1}{3}}(\partial V_0/\partial P)_T/(\partial V/\partial P)_T]$$

is determined from values for the volume at atmospheric pressure, and the values so obtained are used to calculate the compressibility. With the values for the compressibility, V, V_0 and $[1-(V/V_0)^{\frac{1}{3}}(\partial V_0/\partial P)_T/(\partial V/\partial P)_T]$ available it becomes possible to compute $(\partial V_0/\partial P)_T$ as a function of temperature. If the interpretation we have given this quantity is correct it should be a constant, independent of temperature, and equal to the value of $V\beta$ for the liquid at the melting point. Table II shows how nearly this is true. The value of $V\beta$ at the melting point is 55.5×10^{-6} ml/mole/atmos. while the average value of the same quantity as computed indirectly is 56.3×10^{-6} ml/mole/atmos. and the average deviation from this mean value is only 0.7 percent. It may also be pointed out that at least for mercury it is not necessary to utilize compression results directly in order to obtain good values for the constants in the partition function, since at the melting point the term

$$[1-(V/V_0)(\partial V_0/\partial P)_T/(\partial V/\partial P)_T]$$

becomes equal to zero and we are left with

$$PV^{\frac{1}{3}}+a/V^{4/3}=(cd/3)\exp(-cV^{\frac{1}{3}}), \quad (24)$$

an expression which may be used to determine the constant, c, from the volume of the liquid at the melting point. This makes possible the calculation of compressions and compressibilities from vapor pressures and volumes at atmospheric pressure with a considerable degree of accuracy.

Calculation of heats of vaporization and vapor pressures from compressions alone

We have shown how it is possible to put vapor pressures and compressions into one self-consistent scheme and a method for calculating pressure results from vapor pressures has been indicated. The converse calculation of vapor pressures from compressions is quite possible, and indeed may prove to be a fruitful method for substances of very low vapor pressures, e.g., gallium. In order to get an estimate of the accuracy to be expected from such a procedure the constants in an equation of the form

$$V^{\frac{1}{3}}=A\log(P+(B+CT)/V^2)+D \quad (25)$$

were evaluated from Bridgman's data at 0° and at 20°. The constants A, B, C and D were then related to those in the static energy equation (15) by analogy to Eq. (22). Since the depth of the minimum in the potential curve, $E(V)$, plus the zero point energy should represent the heat of vaporization at $T=0$ this is one check that may be used. It was found that the compression results gave a value of 16.6 kcal. for this value. Kelley[16] gives 15.0 for ΔH of evaporation extrapolated to $T=0$ and 15.3 for ΔE_0^0, the discrepancy between these two results being an indication of the probable accuracy of the experimental values. The value 16.6 may also be compared with the more accurate value of 15.30 for the same quantity obtained by using both the vapor pressure and the compressions. The static energy constants obtained by Eq. (25) may also be applied to the calculation of vapor pressures. Thus a value for the vapor pressure of mercury at the melting point is obtained which is too small by a factor of about 5, this discrepancy in the vapor pressure being considerably greater than that in the energy of vaporization since the energy of vaporization occurs as a large exponential term in the expression for the vapor pressure. It is thought that the agreement between the observed heat of vaporization and vapor pressures, and those calculated from the compressions alone is quite satisfactory and indicates that the method may be usefully applied in certain cases. The differences are thought to be entirely due to

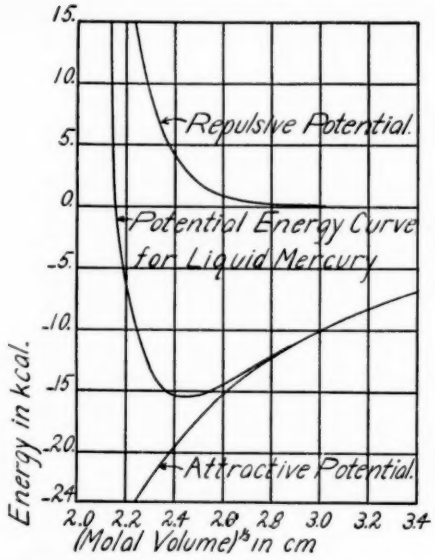

FIG. 3. Potential energy function at zero absolute for liquid mercury minus 3/2 $h\nu$ (0.24 kcal. at minimum).

the roughness of the method of calculation employed, and to the lack of sensitivity of the constants to the data.

Comparison of metals and nonmetals

Hildebrand[15] has pointed out that the difference in the thermodynamic behavior of metals and nonmetals may be attributed to the strong repulsive forces operating in the liquid metals. In agreement with this view we note by inspection of Fig. 3 that at the volume equal to that of the liquid at its melting point at atmospheric pressure the repulsive energy is 19 percent of the total static energy and 16 percent of the attractive energy. At the volume the liquid occupies at its boiling point these figures have dropped to 12 percent and 10 percent, respectively. It is only at a volume of about 20 cc corresponding to a temperature of about 1500°K, 900° above the boiling point, that these figures have dropped to a value as low as 3 percent. The contribution of the repulsive energy to the total energy of typical nonmetallic liquids at low pressures and temperatures is probably even below this low value.

Generalization to include high temperatures and large volumes. Critical properties

It is of interest to inquire if the static energy as found here for mercury may be applied without change to the equation of state developed by Hirschfelder, Stevenson and Eyring.[3] The equation is

$$P+\frac{\partial E(V)}{\partial V}=\frac{RT}{V}[1+b/V+5/3(b/V)^2 +0.2869(b/V)^3+0.1928(b/V)^4], \quad (26)$$

where b is related to that in van der Waals' equation of state and is given by using the equation

$$b=4N4/3\pi d^3/8 \quad (27)$$

and identifying our Eq. (16) for the partition function of a liquid with Eq. (1) and (8) of Eyring and Hirschfelder[2]

$$F_l=N8\left[\left(\frac{V}{N}\right)^{\frac{1}{3}}-d\right]^3\frac{(2\pi mkT)^{\frac{1}{2}}}{h^3}\exp\left(\frac{\Delta E}{RT}\right). \quad (28)$$

For the two expressions to be consistent we must have:

$$2\left(\frac{V}{N}\right)^{\frac{1}{3}}-2d=\frac{kT/h\nu}{(2\pi mkT)^{\frac{1}{2}}/h} +2\left(\frac{V}{N}\right)^{\frac{1}{3}}-2\left(\frac{V_0}{N}\right)^{\frac{1}{3}}, \quad (29)$$

from which it follows that

$$\left(\frac{b}{2}\right)^{\frac{1}{3}}=\left(\frac{\pi}{3}\right)^{\frac{1}{2}}\left[V_0^{\frac{1}{3}}-\frac{N^{\frac{1}{3}}}{2\nu}\left(\frac{kT}{2\pi m}\right)^{\frac{1}{2}}\right]. \quad (30)$$

Values of b were obtained from this formula and substituted into Eq. (26). The observed and calculated volumes are shown in Table IV.

It will be noted that the calculated curve almost exactly parallels the observed one, but is displaced from it by about 0.65 cc. Inspection of Eq. (26) shows that both the left and right-hand

TABLE IV. *Comparison of observed orthobaric volumes with those calculated by Eq. (26).*

$T°$	b cc	V (calc.) cc	V (exp.) cc	V (obs. −calc.) cc
234	26.0	15.33	14.65	−.68
373	25.0	15.7	15.03	−.67
630	24.0	16.4	15.75	−.65
903	23.2	17.2	(16.6)*	(−.6)
1273	22.2	18.2	—	—

* Extrapolated.

sides will disappear together at low pressures only if the minimum in the function $E(V)$ comes at a volume corresponding to that of the liquid at $T=0$. However, the condition that we have previously imposed that

$$P+a/V^2=(cd/3V^{\frac{1}{3}})\exp(-cV^{\frac{1}{3}})$$

fixes the minimum in the curve at a volume equal to that of the liquid at the melting point at low pressures, since

$$a/V^2-(cd/3V^{\frac{1}{3}})\exp(-cV^{\frac{1}{3}})$$

is simply $\partial E(V)/\partial V$. Thus we expect Eq. (26) to be inconsistent by an amount about equal to the expansion from $T=0$ to the melting point, which is just what we observe. It is expected that further work will eliminate the difficulty.

Since we have a means available for getting van der Waals' constants a and b, it should be possible to compute approximate values for the critical constants by using the relations

$$T_c=8a/27\,\mathrm{Rb} \qquad \text{and} \qquad P_c=a/27b^2.$$

On substitution of the values 11.172×10^6 and 21.0 cc for a and b, respectively, the values, 1900°K and 950 atmos. are obtained for the critical temperature and pressure to be compared to the experimental values of 1800°K and 1000 atmos.[19] Convesrely the value 9.0×10^6 is obtained for a from the critical temperature and pressure. The agreement between the a value obtained from the critical constants and that from the vapor pressure gives us added confidence in the validity of the form chosen for $E(V)$. This agreement is particularly interesting since the bonding in metallic solids and liquids is usually thought of as quite different from the van der Waals forces acting between a pair of molecules. Although we expect Eq. (26) to give better values than van der Waals' equation for the critical phenomena we have not carried through the rather laborious calculations.

[19] Landolt-Börnstein, *Tabellen*.

Further applications

If vapor pressures are available it seems a procedure somewhat similar to that outlined for liquids might be used to get empirical information about the lattice energy of solids. Hitherto[20] a scheme based on compressions alone has been used to get the variation of lattice energy with volume, but our results for liquid mercury indicate that more accurate results may be obtained if other thermodynamic properties are considered as well. A further improvement in the results obtained would no doubt follow any improvement in the form for representing static energy as a function of volume. Our present form certainly yields remarkably satisfactory results, however.

Further applications of the method developed here are being made in this laboratory and the results will be reported at an early date along with some more theoretical aspects of the subject.

[20] Reference 5, p. 23.

LETTERS TO THE EDITOR

This section will accept reports of new work, provided these are terse and contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section must reach the office of the Managing Editor not later than the 15th of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge ($3.00 per page) will not be made and no reprints will be furnished free.

On the Electrolytic and Chemical Exchange Methods for the Separation of the Lithium Isotopes

A number of methods have been used in attempts to separate the lithium isotopes of mass 6 and 7. Early attempts by means of the mass spectrograph gave only minute quantities. However, Rumbaugh and Hafstad[1] have recently obtained sufficient quantities of the two isotopes by this method for a study of some of their nuclear properties. Kendall and Crittenden[2] attempted a separation by means of electrical mobility without success. Encouraged by the successful separation of the hydrogen isotopes by electrolysis, a number of investigators have started work on similar methods using a flowing mercury cathode. Eucken and Bratzler[3] have reported some experiments on the electrolysis of a lithium sulphate solution. The experimental error in the atomic weight determinations used to estimate the change in isotope ratio was practically as large as the effect observed. The value reported for the fractionation factor is therefore of doubtful accuracy.

Lewis and Macdonald[4] have secured a striking increase in the concentration of Li^6 by using a counter-current extraction process which depended upon a difference in the distribution coefficients of the lithium isotopes between an ethyl alcohol solution of lithium chloride and a lithium amalgam. During the past year we have investigated two possible methods of effecting partial separations of the lithium isotopes, one depending upon a possible electrolytic separation, and the other a difference in distribution of the lithium isotopes between a solid material and a liquid solution.

In investigating the feasibility of the electrolytic method for separating lithium isotopes, we have used the electrolysis of a large quantity of lithium hydroxide down to a small residue. The object of this experiment was to determine the simple process fractionation factor, a knowledge of which is essential for the use of the method. The electrolytic cell consisted of a fluted nickel anode placed about 1 cm above a mercury cathode. This nickel anode was made by spot welding together strips of nickel bent such that the finished anode was a honey-cone shape. The mercury was stirred rapidly with a glass stirring device to give a uniform surface. The electrolysis vessel was surrounded by a water-cooling jacket to enable us to keep the temperature approximately controlled in the neighborhood of 25°C. Mercury from a separatory funnel was allowed to flow continuously into the cell and out through a gooseneck tube in order to maintain the level of the mercury constant and to remove the lithium amalgam as it was produced. The lithium was removed from the amalgam with the formation of lithium hydroxide by allowing it to flow in a counter-current fashion with water over nickel rings under which condition hydrogen was generated due to formation of local couples. The cell was operated with a current density of 0.62 amperes per square centimeter of mercury surface. The procedure was to fill the cell with 800 cc of a 10 percent lithium hydroxide solution and electrolyze until about one gram of lithium hydroxide was left in the cell. When 20 such runs were completed, the residual solutions were united, concentrated, and electrolyzed further. From titrations of the original and final solutions against standard acid, the ratio of the initial to the residual lithium was found to be approximately 600.

The isotopic composition of the initial material and the final residue were determined by A. Keith Brewer, using his mass spectrometer. The ratio of Li^6 to Li^7 in ordinary lithium is 1 to 11.6, according to his determination. However, the lithium hydroxide used in these experiments was found to have an isotopic ratio of 1 to 12.5, though a sample of lithium from a commercial lithium bromide showed the normal abundance. The isotopic ratio of the final solution remaining in the electrolytic cell was 1 to 14.2, showing that Li^6 is electrolyzed preferentially with respect to Li^7. Using the Rayleigh distillation formula

$$\left(\frac{1-N_0}{1-N}\right)^{1/\alpha-1}\left(\frac{N}{N_0}\right)^{\alpha/\alpha-1}=\frac{W_0}{W},$$

which applies to such processes, we find that the simple process fractionation factor, α, is 1.020. This is very small compared to the values of 3 to 10 for the fractionation factor of hydrogen and deuterium. Lewis and Macdonald estimated that the fractionation factor from their results was approximately 1.025. This factor, of course, applies to the distribution between ethyl alcohol as a solvent and the mercury amalgam. This should check our result only if the relative solubilities of the Li^6 and Li^7 isotopes are the same in water and in ethyl alcohol.

We attempted a concentration of the lithium isotopes by extracting a water solution of lithium bromide with methylamyl alcohol and reduced the concentration in the water solution by a factor of 20 to 1. The residue showed no difference in isotopic ratio to the original material. Also, we extracted a solution of lithium bromide in methyl-

amyl alcohol with water and reduced the concentration by a factor of 1000 to 1, and likewise found no change in the isotopic ratio between the original material and the residue. This shows that the relative solubilities of the isotopes of lithium are very nearly the same in methylamyl alcohol and water. It seems probable that the solubilities of the lithium isotopes in ethyl alcohol and water are likewise nearly the same, and if this is true our enrichment factor in the electrolysis may be regarded as a check on the results of Lewis and Macdonald. The slight discrepancy between the two figures is probably within the experimental limits of error of either work, and indicates that we secured in our electrolysis only the equilibrium increased concentrations with no evidence for a kinetic effect as is found in the case of the separation of hydrogen and deuterium. Of course, it may be that kinetic effects will be important at high current densities and correspondingly increase the fractionation factor.

It is an interesting fact that the two samples of commercial lithium compounds should have markedly different isotopic ratios. It would appear that somewhere in the process of manufacture an appreciable separation of the isotopes of lithium occurred. It is difficult to see how this could occur in the usual commercial process since commercial methods usually produce a fairly high percentage of the element present in the crude material in the form of the final product, and if this is done no fractionation could be expected. One method commonly used to extract lithium from some of its complex aluminum silicate ores is to heat the ore with potassium sulphate. A zeolite type reaction takes place in which the potassium replaces the lithium. This replacement may possibly be preferential with respect to one isotope. For this reason we thought that it would be of interest to investigate the exchange of the lithium isotopes between Permutite and solutions of alkali metal salts. For this purpose the Permutit Company kindly furnished some of their Permutite which is a complex sodium aluminum silicate of the zeolite type and has a comparatively high percentage of replaceable sodium.

In order to determine the approximate value of the simple process fractionation factor, a batch containing 300 g of lithium chloride in a twenty percent solution was extracted with a large number of successive 30 g portions of the zeolite. After each addition the mixture was shaken vigorously for 20 minutes before filtration in order to allow equilibrium to be established. At various intervals the sodium chloride resulting from the replacement of the sodium ion from the Permutite was separated. When the lithium chloride had been reduced by a factor of 70, the lithium chloride was converted to the carbonate and analyzed by A. Keith Brewer. The ratio of the two isotopes had changed from 11.6 to 12.7. Using the Rayleigh formula for an approximation, one gets 1.022 for the fractionation factor. It is difficult to estimate the accuracy of this value or its exact meaning because of the variable concentration of the sodium ion and the lithium ion in the solution being extracted. Rate processes may also be important. However, similar conditions will occur in the operation of a column so one may consider the above value as a fair approximation. This is small and one cannot expect appreciable separation unless counter-current methods are employed. These fractionation factors are very close to one calculated by Urey and Greiff[5] for another reaction showing that their estimate of these fractionation factors is approximately correct.

A number of experiments were run in which a dilute lithium chloride solution was run slowly through a 35-foot column of the zeolite contained in a 3/4-inch stainless steel pipe. In one such experiment the first lithium chloride through the column gave the ratio 13.3 or a change of about 15 percent. From these experiments it seems that the lighter isotope is preferentially held by the zeolite. Similar experiments were made using a solution of ammonium chloride. The first ammonium chloride through the column was converted to nitrogen and analyzed with the mass spectrometer by Marvin Fox in this laboratory. The ratio of $N_{14}N_{14}$ to $N_{14}N_{15}$ in ordinary nitrogen was 124 to 1 while the ratio in the product obtained was 137 to 1 or a change of about 10 percent. It is to be noted that in the case of the ammonium ions, the one containing the heavier isotope seemed to be preferentially held by the zeolite while the lighter isotope of lithium is more strongly held. It is difficult to say what may account for this difference in behavior. The difference, however, may aid in determining the mechanism which is responsible for the separation of the isotopes. It is hoped that an appreciable fractionation of a number of isotopes may be achieved using zeolite or other suitable adsorbing substances much as is done in the separation of closely related organic compounds by the recently developed methods of chromatographic analysis.

The authors express their thanks to Dr. A. Keith Brewer of the Nitrogen Fixation Laboratory for the analyses which he has so kindly made, to the Permutit Company for supplying the Permutite for these experiments, and to Dr. John G. Dean of the Permutit Research Laboratories for his useful discussions and suggestions.

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H. C. Urey

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June 14, 1937.

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Corrections to: The Properties of Paraffins II

(J. Chem. Phys. **5**, 264 (1937))

Formula (1): $Q=Q_0(1-T/T_c)0.4$ should read:

$$Q=Q_0(1-T/T_c)^{0.4}.$$

In the heading of column 6, Table VII, Q_b from gas should read: Q_b from Q_{Av}. Page 266, right column, line 30: the power of U should read: the power of n. Formula (7): $Q_B/T_B=8.97\times n^{0.25}+n^{8.99/0.17}$ should read:

$$Q_B/T_B=8.97\times n^{0.25}+8.99/n^{0.17}.$$

A. H. W. Aten, Jr.

Hilversum, Netherland,
June 4, 1937.

The Infrared Spectrum and Internuclear Distances of Methyl Acetylene*

A parallel type band of methyl acetylene in the photographic infrared has recently been investigated by Herzberg, Patat and Verleger[1] who were able to obtain from it an accurate value of the large moment of inertia of the molecule. Assuming that all parameters except the C−C single bond distance have the values which have been found in other molecules they were obliged to conclude that this distance is about 1.463A. This conclusion seems rather remarkable since the C−C single bond distance has been found to be approximately 1.54A in a number of molecules, and it seemed worth while to check the result.

We have obtained very satisfactory pictures of the methyl acetylene band at λ10,304, completely free from contamination by acetylene, in which the lines are visible right down to the origin except the first line of the P branch which is obscured by the strong Q branch. The lines have been measured by one of us directly on two plates and by the other on microphotometer curves of the same plates. The results are very self-consistent and agree well with those of the authors mentioned above. Indeed we even check quite well the measurements on lines near the origin of the band and in the vicinity of $J=23$ so that the deviations of the points for these regions from the straight line of Fig. 2 of H. P. and V.[1] appear to be due to some systematic error which is duplicated in our work, and not to accident.

From the average of our two independent measurements and those of H. P. and V. we obtain as the most probable values for the rotational constants, $B'=0.28231$ and $B''=0.28496$. These differ from those given by H. P. and V. by little more than their estimated error and leave the situation unchanged as regards the internuclear distances.

We have carefully considered various errors which might have entered into the measurements and their interpretation. The origin of the band appears to be uniquely determined by the Q branch but aside from this we believe we could pick the band center from the intensity distribution with an error of not more than two lines. The relative line numbering of the two branches also appears to be unique since the lines are visible clear down to the origin with one exception. Furthermore any other relative numbering leads to rotational constants which change more rapidly with J than is possible.

We have considered possible errors due to the contamination of the λ10,304 band by two weak bands which appear to arise from absorption by molecules in excited vibrational levels. Of these only the Q branches are visible and one is so weak that it can scarcely cause any disturbance except in its Q branch which makes the measurement of one line a little uncertain. The other, however, may possibly be as much as one-fifth as intense as the main band and appears to introduce some error in the measurement of lines near the origin of the latter. As mentioned above, the measurements of the lines with $J<8$ appear to be systematically in error which might well be expected since they are very weak while the R branch of the overlying satellite band is near its maximum of intensity in this region. In the remainder of the measurements we do not find any evidence of appreciable errors of the same sort. In the R branch the lines with $J>15$ should in any case be practically free from contamination, while in the P branch if the lines of the satellite band are strong enough to cause any disturbance we should expect the errors to alternate between negative and positive owing to the inequality of spacing of the main and satellite branches. Consequently the calculated rotational constants should also fluctuate, though the average value should be about correct. There seems to be no indication that this state of affairs exists and in comparing measurements with the line positions calculated from the average rotational constants one finds no evidence of special error in the P branch except possibly in a little region about $J=23$.

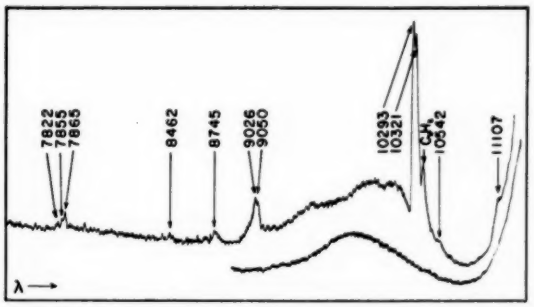

FIG. 1. The upper curve is a microphotometer tracing of the absorption spectrum of methyl acetylene in the photographic infrared taken under low dispersion. The wave-lengths of several maxima which appear to belong to bands of parallel type are given. The broad maximum in the region λλ9000–10,000 is mainly due to a minimum in the plate sensitivity, as shown in the lower curve which gives the plate background, but it is possible that there may be two weak bands in this region, probably of perpendicular type.

Consequently we are obliged to regard the short C−C distance in methyl acetylene as real. This result does not appear to us particularly surprising. In the first place, as has been known for some time, the C−H distance in acetylene is appreciably shorter than in methane. In the second place, in some considerations regarding the spectra of the substituted acetylenes made by one of us[2] it seemed necessary to assume that the C−C single bond force constant in dimethyl acetylene, etc., is somewhat larger than would be compatible with a distance of 1.54A.

It would of course be very desirable to make measurements on other bands of methyl acetylene but we have not found it possible to do so with high dispersion. Under low dispersion we have observed a number of bands which are shown in the accompanying microphotometer tracing. One of these, at λ9040, is moderately strong and appears to be of the same type as the λ10,304 band but it was just too weak to show up in spectrograms taken with the 21 ft. grating with the amount of material we had available.

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May 10, 1937.

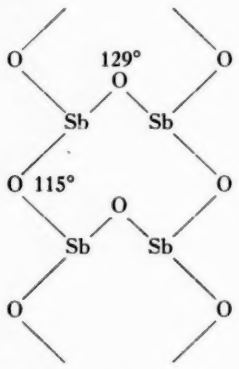
* The experimental work here described was a part of a program of research made possible by a grant-in-aid from the National Research Council to one of us (R. M. B.). We are indebted to Mr. H. D. Springall for the methyl acetylene used in the investigation.

[1] Herzberg, Patat and Verleger, J. Phys. Chem. **41**, 123 (1937).
[2] R. M. Badger, J. Chem. Phys. **5**, 178 (1937).

Polymorphism of Antimony Trioxide and the Structure of the Orthorhombic Form

Vapor density measurements indicate that antimony trioxide vapor below 1000°C consists principally of Sb_4O_6 molecules. These molecules also have been shown to be present in the crystalline cubic form of this compound[1] which is stable below 570°C.[2] Crystal structure analysis of the high temperature orthorhombic modification which can be obtained as a metastable phase at room temperature, however, leads to a structure of an entirely different type in which such molecules have lost their identity.

The structure of this orthorhombic form as here reported can be considered as made up of double molecular chains of the following type:



with their axes parallel to the crystallographic c axis. Each antimony atom is at the expected distance, 2.00 to 2.02A, corresponding to electron pair binding[3] from three oxygen atoms of the double chain. Absence of such binding between the chains results in perfect cleavage parallel to them.

That the antimony oxygen binding is really of a directed type as would be expected from electron pair binding is further shown by the observed valence angles. The valence angles of oxygen atoms within a single chain are *ca.* 115° while the corresponding angles for those oxygen atoms connecting the single chains to form the double ones are about 129°. These values are similar to those found in other simple compounds containing oxygen, the variation being from about 100 to 130° where ring formation does not limit it. The antimony valence angles, which are 79, 92 and 100°, also have about the expected values.

Since transition of the cubic to the orthorhombic form involves destruction of Sb_4O_6 molecules by rearrangement of electron pair bonds it might be expected to require considerable activation energy. This accounts for the slowness of the transition and the persistence of the orthorhombic form as a metastable phase.

The crystal structure is summarized as follows: space group $Pccn-D_{2h}^{10}$, $4Sb_2O_3$ in the unit of structure with $a=4.92$A, $b=12.46$A, $c=5.42$A. Antimony and two-thirds of the oxygen atoms are in the general positions with $x_{Sb}=0.044_4$, $y_{Sb}=0.128_3$, $z_{Sb}=0.176_4$, $x_0=0.150$, $y_0=0.05_8$, $z_0=-0.14_1$. The remaining oxygen atoms are on the twofold axes at $\frac{1}{4}\ \frac{1}{4}\ u$ with $u_0=0.015$. These parameter values were determined on pure materials from intensity data alone without assumption of possible structure type.

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May 24, 1937.

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[2] Roberts and Fenwick, J. Am. Chem. Soc. **50**, 2125 (1928).
[3] Pauling and Huggins, Zeit. f. Krist. **87**, 218 (1934).

On the Assignment of the $\delta_{\pi s}$, $\nu_{2\pi s}$ Frequencies in Ethylene Molecule

The assignment of the fundamental frequencies of C_2H_4 has been given by a number of authors.[1] Of the five "parallel" vibrations $\nu_{\pi s}$, $\nu_{\pi a}$, $\delta_{\pi s}$, $\delta_{\pi a}$, $\nu_{2\pi s}$, one can be quite certain that $\nu_{\pi s}=3019$ (Raman), $\nu_{\pi a}=2988$ (infrared), $\delta_{\pi a}=1444$ (infrared). For $\delta_{\pi s}$ and $\nu_{2\pi s}$, there seem to be two possible choices. Sutherland and Dennison[1] assumed $\delta_{\pi s}=1623$ (Raman), $\nu_{2\pi s}=1342$ (Raman), while Mecke and others[1] favor the alternative $\delta_{\pi s}=1342$, $\nu_{2\pi s}=1623$. As these two vibrations have the same symmetry character and enter symmetrically in any system of equations for the calculation of the force constants, it is not possible to decide between these two assignments from polarization data in the Raman effect or from the determinantal equations giving these frequencies. This can be done, however, by examining the transformation equations between the physical coordinates and the normal coordinates for these vibrations.

Following Sutherland and Dennison,[2] we shall introduce the coordinates x_1 for the relative displacement along the C=C axis of the center of gravity of the two H atoms and the C atom in one CH_2 group x_2 for the similar displacement in the other CH_2 group, x_0 for the relative displacement between the two C atoms, q_1, q_2 for the relative displacements between the two H atoms in each group in the direction perpendicular to the C=C axis. These coordinates serve for describing the five vibrations whose frequencies are given by the determinantal equation

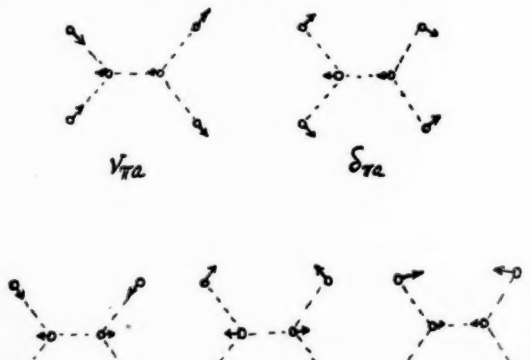

FIG. 1. "Parallel" vibrations of C_2H_4.

$$\begin{vmatrix} A\lambda-a & B\lambda & C\lambda & -d & 0 \\ B\lambda & A\lambda-a & C\lambda & 0 & -d \\ C\lambda & C\lambda & D\lambda-c & 0 & 0 \\ -d & 0 & 0 & \frac{C}{2}\lambda-b & 0 \\ 0 & -d & 0 & 0 & \frac{C}{2}\lambda-b \end{vmatrix}=0, \quad (1)$$

where a, b, c and d are force constants defined in Sutherland and Dennison's paper, and

$$A=\frac{2m(m+M)}{2m+M}, \quad B=\frac{2m^2}{2m+M}, \quad C=m, \quad D=\frac{2m+M}{2}.$$

That their treatment of these vibrations is satisfactory is shown by the fact that the five observed frequencies satisfy quite well the relation which results on eliminating the four force constants among the five equations from (1). The modes of these vibrations are shown in Fig. 1.

To decide between the two assignments $\begin{cases}\delta_{\pi s}=1342\\ \nu_{2\pi s}=1623\end{cases}$ and $\begin{cases}\delta_{\pi s}=1623\\ \nu_{2\pi s}=1342,\end{cases}$ let us denote the normal coordinates by ξ_i, $i=1, 2, \cdots, 5$. The transformation equations between the coordinates x_1, x_2, x_0, q_1, q_2 and these normal coordinates are then

$$x_1=\Sigma c_{1i}\xi_i, \quad x_2=\Sigma c_{2i}\xi_i, \quad x_0=\Sigma c_{3i}\xi_i, \quad q_1=\Sigma c_{4i}\xi_i, \quad q_2=\Sigma c_{5i}\xi_i,$$

where $c_{1i}\cdots c_{5i}$ are proportional to the minors of the elements in any one row in the secular determinant (1) in which λ is given the value of the ith root, i.e., of the ith normal vibration. For the ith vibration, we have, except for a common factor of proportionality,

$$x_1=\begin{vmatrix} A\lambda_i-a & C\lambda_i & -d \\ C\lambda_i & D\lambda_i-c & 0 \\ -d & 0 & \frac{C}{2}\lambda_i-b \end{vmatrix}\xi_i,$$

$$x_2=-\lambda_i\left(\frac{C}{2}\lambda_i-b\right)\begin{vmatrix} B & C \\ C\lambda_i & D\lambda_i-c \end{vmatrix}\xi_i, \quad (2)$$

$$x_0=C\lambda_i\begin{vmatrix} B\lambda_i & A\lambda_i-a & -d \\ 1 & 1 & 0 \\ 0 & -d & \frac{C}{2}\lambda_i-b \end{vmatrix}\xi_i,$$

$$q_1=d\left(\frac{C}{2}\lambda_i-b\right)^{-1}x_1, \quad q_2=d\left(\frac{C}{2}\lambda_i-b\right)^{-1}x_2.$$

From these, the relative values of the coordinates x_1, x_2, x_0, q_1, q_2 for the five fundamental frequencies can be obtained. The result is given in Table I. Consideration of the vibrational form of $\delta_{\pi s}$ (Fig. 1) shows that x_1/x_0 and x_2/x_0 must be negative, while q_1/x_0, q_2/x_0 must be positive. These relations are satisfied only by the frequency 1623 cm^{-1}, while the relative displacements for the frequency 1342 cm^{-1} are compatible with $\nu_{2\pi s}$, if the amplitudes of the H atoms are larger than those of the C atoms, and if on approaching together of the two CH_2 groups the H atoms in each group are pushed apart a little, as shown in Fig. 1.

TABLE I. *Relative displacements in the normal vibrations of C_2H_4.*

	2988 cm^{-1}	1444 cm^{-1}	3060 cm^{-1}[3]	1623 cm^{-1}	1342 cm^{-1}
x_0	0	0	$\neq 0$	$\neq 0$	$\neq 0$
x_1/x_2	-1	-1	1	1	1
q_1/q_2	-1	-1	1	1	1
x_1/x_0 or x_2/x_0	—	—	<0	<0	>0
q_1/x_0 or q_2/x_0	—	—	<0	>0	<0
x_1/q_1	>0	<0	>0	<0	<0
assignment	$\nu_{\pi a}$	$\delta_{\pi a}$	$\nu_{\pi s}$	$\delta_{\pi s}$	$\nu_{2\pi s}$

But these are just what one would expect on purely mechanical considerations. Thus we are led to the assignment of Sutherland and Dennison, namely, $\delta_{\pi s}=1623$, $\nu_{2\pi s}=1342$ in contradiction to that of Mecke.

In view of this change, the values of the frequencies for C_2H_4, *cis*, *trans* and asymmetric $C_2H_2D_2$, C_2D_4 given in another article "On the Fundamental frequencies of CH_2, CHD, CD_2, CHCl, CDCl and *Cis* and *Trans* $C_2H_2D_2$ and $C_2H_2Cl_2$"[4] should be interchanged. This does not, however, necessarily invalidate the usual assignment to the vibration $\nu_{2\pi s}$ of frequencies in the region 1500–1600 cm^{-1} in molecules in which one or more H atom is replaced by another atom or a group of atoms. The frequency of the vibration $\nu_{2\pi s}$ depends not only on the force constant between the double bond carbon atoms, but also on the force constants and masses in the CH_2, CHX, or CX_2 group.

In Table I, the signs for the ratios x_1/q_1 are obtained from Eq. (2) with the positive sign for d, i.e., $d=+1.46\times10^5$. Consideration of Fig. 1 shows that the signs of x_1/q_1 for all the five vibrations are just as expected. Thus we are led to choose the positive value for d, in agreement with the conclusion of Sutherland and Dennison based on a different reason.[1]

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National University of Peking, Peiping,
March 22, 1937.

[1] G. B. B. M. Sutherland and D. M. Dennison, Proc. Roy. Soc. **A148**, 250 (1935); R. Mecke, Zeits. f. physik. Chemie **B17**, 1 (1932); *Hand und Jahrbuch d. chem. phys.*, Bd. 9/II, 395 (1934); Bonner, J. Am. Chem. Soc. **58**, 34 (1936).

[2] Sutherland and Dennison, Proc. Roy. Soc. **A148**, 250 (1935). Reference is made to this paper for the notation and values of the force constants used in this letter.

[3] It is found that a change of the value 3019 to 3060 is necessary in order to satisfy the relation (5) in Sutherland and Dennison's paper and hence to give consistent solution for the force constants.

[4] J. Chem. Phys. **5**, 392 (1937).

The Viscosity (or Fluidity) of Liquid or Plastic Monomolecular Films

Theories of the structure of monomolecular films are in an unsatisfactory state on account of a lack of knowledge of the change of properties of the films as the film pressure (f) increases. A determination of the viscosity relations of the films would be of great value, not only to the theory, but also in connection with the phenomena of penetration of liquids into solids, and of the rate of spreading of films. Unfortunately the literature contains no values for the viscosity of liquid films. In the work reported here such vis-

TABLE I. *Viscosities in surface poises (s. p.) of liquid monolayers at 25° C.*

No. C atoms	Saturated Acids	η in dyne sec./cm	Unsaturated Acid
14	Myristic	0.000161	
15	Pentadecylic	0.000228	
16	Palmitic	0.000248	
17	Margaric	0.000317	
18	Stearic	0.000307	Oleic 0.000162
19	Nonadecanoic	Plastic solid	
20	Arachidic	0.001790	

cosities have been obtained by the use of two new viscosimeters, while a third type has been designed.

1. The capillary slit surface viscosimeter

A transverse slit 5 to 15 cm long, produced by two movable jaws adjusted by a screw, occupies the middle of an ordinary metal barrier, used to compress the film on the surface of a trough filled with water. The film is put on the surface of the water between this barrier and the film balance, which may be of the usual type or a much more simple type recently developed in this laboratory. The slit is usually used at diameters (d) between 0.2 and 1.5 mm, and after being given a very light coat of paraffin, is placed so that it rests just in contact with the surface of the water. The film flows under its own pressure through the slit on the horizontal water surface. The theory developed for this case gave the equation:

$$\eta = \frac{f}{Q}\frac{d^3}{12l}.$$

Q, the quantity of the film which passes through the slit in unit time was found to vary exactly as the cube of the diameter instead of as d^4 in a capillary tube. Some viscosities obtained are given in Table I.

All of these films, with one exception gave a linear f, Q relation and the straight line passed through the origin, so all of these are true liquid films. With nonadecanoic acid the relation was nonlinear and the linear part of the curve did not extrapolate through the origin. The film is therefore a plastic solid. Cetyl alcohol films were investigated both by the capillary slit and torsion viscosimeters, and exhibited the same general behavior with both, as described later. In the less viscous regions these two latter films gave viscosities as low as 0.0019 s.p.

Preliminary work with a small difference of temperature seems to indicate an increase of viscosity with temperature.

At 20°C the viscosities are 0.000162 for oleic acid and 0.000289 for stearic acid, both with 18 carbon atoms, and 0.000142 for myristic acid with 14 carbon atoms. The viscosity is found to be much more dependent upon the tightness of packing of the molecules in the film than upon the number of carbon atoms in the chain.

2. Torsion ring surface viscosimeter

The differential equation of the torsion pendulum gives on integration the angular deflection:

$$\theta = e^{-rT/I}C' \sin\left(\frac{k}{I} - \frac{r^2}{I^2}\right)^{\frac{1}{2}},$$

where r is the damping factor due to the medium, I the moment of inertia of the oscillating system, C' is a constant and k is the wire constant for restoring torque. The amplitude is $C'e^{-rT/I}$ and the period $T=2\pi(I^2/(kI-r^2))^{\frac{1}{2}}$ =const. and for two successive amplitudes $\theta/\theta' = e^{rT/I}$. It can be shown that

$$2.303\Delta = 2.303(\log\theta - \log\theta_1) = rT/I,$$

where Δ is the logarithmic decrement.

With a true liquid film the viscosity is independent of amplitude, and a plot of the logarithm of the amplitude against the number of swings gives a straight line whose slope is a measure of the viscosity. With a plastic solid the line is curved. Thus the torsion ring pendulum is a powerful tool for the indication of changes of structure in a film.

In order to change the sensitivity of the apparatus it is advisable to use different torsion wires. In order to make the results with two different wires comparable it is necessary to compare the ratio of the log decrements at the same film pressure.

With a clean water surface.—

$$2.303(\log\theta_1' - \log\theta_2') = \Delta' = 2\pi r'/(kI-r'^2)^{\frac{1}{2}} = r'T'/I$$

and with the film

$$\Delta'' = 2\pi(r'+r'')/[kI-(r'+r'')^2]^{\frac{1}{2}} = (r'+r'')T''/I$$

or

$$B = \frac{r'+r''}{r'}\cdot\frac{(kI-r'^2)^{\frac{1}{2}}}{(kI-(r'+r'')^2)^{\frac{1}{2}}}.$$

In order to make B larger the value of r'' was increased with respect to r' by soldering a ring with a lower razor edge to the bottom of the circular disk of the torsion pendulum. This greatly increased the sensitivity. For the two wires used kI was 2,304,000 and 50,600 and r'^2 7.37 and 1.88, in units of g^2cm^4 $sec.^{-2}$.

Cetyl alcohol films: on 0.01 m HCl.—The film is very tightly packed, with a molecular area at high pressure of about 19 sq. A. Below the kink point at 13 dynes at 25°C the f, a relation is expressed by a straight line which represents an extremely low compressibility. At all pressures below this kink point the films are true liquids, but the viscosity increases rapidly and almost linearly with the film pressure. Above the kink the compressibility is even less, the film is a plastic solid, and the viscosity increases even more rapidly with the pressure.

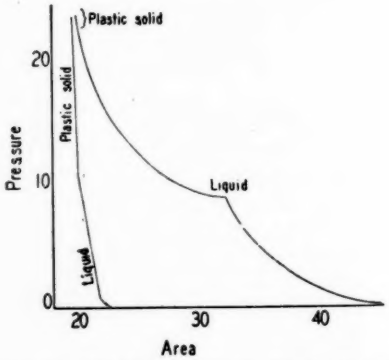

FIG. 1. Pressure area relations with regions and plastic solid films for cetyl alcohol and pentadecylic acid.

Pentadeclyic acids.—This acid forms an expanded film on 0.01 m HCl at 25 degrees. At 0.1 dyne a is 44 sq. A. As the film is compressed it remains liquid, but the viscosity increases to the kink at 9.00 dynes and 32.3 sq. A. Just above this kink the viscosity remains nearly constant as the area decreases and then the viscosity increases more and more rapidly. At about 23 dynes per cm pressure the film changes to a plastic solid.

It is obvious that the intermolecular forces between the molecules in the film have much greater effects when the film is tightly packed than when it is expanded. With the aid of further measurements it is hoped to learn the part played by the forces between the molecules of the film and the underlying water.

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June 11, 1937.